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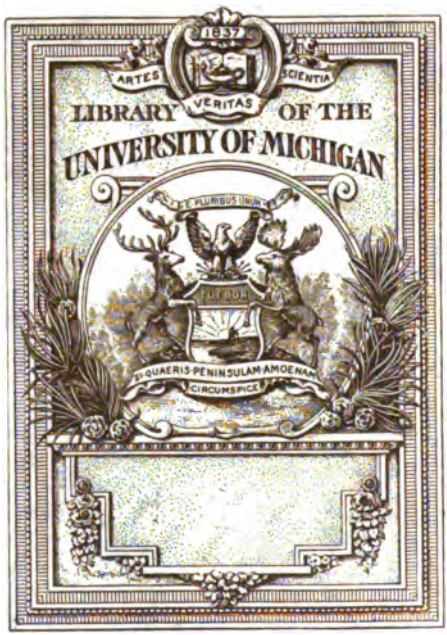
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TRANSACTIONS

OF THE

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VOLUME XVII

Containing the Papers Read at the Meeting Held at Detroit, Mich., February 15, 16, 17, and 18, 1915, Together with Supplementary Discussions and Other Matters.

ARTHUR S. WATTS, *Editor*

This Society is not, as an organization, responsible for the statements of facts or opinions expressed in these papers and discussions.

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BEECHER, MILTON F., Worcester, Mass.	Refractory Engineer, Research Laboratories, Norton Company
BELL, FRED SMITH, 1318 Wright Bldg., St. Louis, Mo.	Vice President, The Mandle Clay Mining Company
BELL, M. LLEWELLYN, B.S., 407 Franklin Ave., Wilkinsburg, Pa.	Carnegie Steel Company, Braddock Pa.
BENTLEY, LOUIS LEES, M.E., Beaver Falls, Pa.	Superintendent, Armstrong Cork Company
BERRY, CHARLES W., St. Louis, Mo.	Chemist, Laclede - Christy Clay Products Company
BEST, HEROLD A., P. O. Box 35, Haydenville, Ohio	National Fireproofing Company
BISH, HOWARD A., Carey, Ohio	Assistant Superintendent, National Electric Porcelain Company
BISSELL, GEORGE FRANCIS, Ottawa, Ill.	Chicago Retort and Fire Brick Company.
BLACKMER, EDWARD LESLIE, 501 Clara Ave., St. Louis, Mo.	Assistant Superintendent, Blackmer and Post Pipe Company
BLAIR, MARION W., M.E., Kushequa, Pa.	Superintendent Kushequa Brick Company
BLAIR, WILLIAM P., Cleveland, Ohio	Secretary, National Paving Brick Manufacturers' Association
*BLAKE, CHAS. GLENVILLE, M.E., Pittsburgh, Pa.	Engineer and Salesman, Armstrong Cork Company
BLOOMFIELD, CHARLES A., Box 652, Metuchen, N. J.	Treasurer, Bloomfield Clay Company
BOECK, PERCY A., 434 W. 120th St., New York, N. Y.	Chemical Engineer
BOORAEM, J. FRANCIS, M.E., and E.E., 1182 Broadway, New York, N. Y.	Treasurer and Manager, American Enameled Brick and Tile Company
BOOZE, MACDONALD CHARLES, Sullivan, Ill.	Student in Ceramics, University of Illinois
BOW, LOREN CUSHING, 116 Sylvester St., Detroit, Mich.	Student in Ceramics, University of Illinois
BOWMAN, ROBERT K., Trenton, N. J.	Treasurer, Trenton Fireclay and Porcelain Company
BOWMAN, WILLIAM J. J., C.E., Trenton, N. J.	Trenton Fireclay and Porcelain Company
BRADY, HUGH SOBESKI, Wheeling, W. Va.	Engineer, Hazel Atlas Glass Company

* Died April, 1914.

BRAGDON, WILLIAM V., B.Sc. (in Cer.) 4424 Delmar Ave., St. Louis, Mo.	Ceramic Division, Academy of Art, University City
BRAND, JOHN JULIUS FREDERICK, 723 Camp St., Sandusky, Ohio	Superintendent, Hinde Brick and Tile Company
BRANDT, GEO. F., Box 314, Minerva, Ohio	Clay Shop Foreman, Owen China Company
BRAY, ARCHIE C., CR.E., Helena, Mont.	Assistant Superintendent, General Ceramic Work, Western Clay Manufacturing Company
BRIGGS, LEONARD S., South River, N. J.	National Fireproofing Company
BROMBERG, NATHAN, B.S., 1330 Washburne Ave., Chicago, Ill.	Student in Ceramics, University of Illinois
BROWER, FRED., CR.E., Hebron, North Dakota	Hebron Fire and Pressed Brick Company
BROWN, EDMUND, Perrysburg, Ohio	General Manager, Edward Ford Plate Glass Company
BROWN, L. K., Zanesville, Ohio	Vice President, The Burton Townsend Company
BROWN, RALPH E., 740 Pearl St., Ottawa, Ill.	Chicago Retort and Fire Brick Company
BROWN, RICHARD L., Wayne Junction, Philadelphia, Pa.	President, Brown Instrument Company
BRUNER, WILLARD LYNN, 196 Water St., Perth Amboy, N. J.	Ceramic Chemist, Roessler and Hasslacher Chemical Company
BRYAN, MERRILL L., Seattle, Wash.	Superintendent, Terra Cotta Department, Denny-Renton Clay and Coal Company
BUCHER, ERMANE GAYLORD, B.S., (in Cer.), 305 E. Greene St., Champaign, Ill.	Student in Ceramics, University of Illinois
BUCKNER, O. S., 23 S. Main St., Newark, N. Y.	Student in Ceramics, University of Illinois
BURR, ROBERT BRINKERHOFF, Columbus, Ohio	Logan Natural Gas and Fuel Company
BUTTERWORTH, FRANK W., Danville, Ill.	General Manager, Western Brick Company
CABLE, DAVIS A., M.E., East Sparta, Ohio	General Superintendent, United States Roofing Tile Company
CABLE, MARGARET KELLY, Grand Forks, N. D.	Instructor in Ceramics, College of Mining Engineering, University of North Dakota
CALDWELL, FRANK WALKER, B.S., in M.E., Lookout Mountain, Tenn.	Chemist, Cast Iron Enamel Work, Cahill Iron Works
CAMPBELL, A. R., Metuchen, N. J.	Federal Terra Cotta Company
CARDER, FREDERIC R., Corning, N. Y.	Manager and Chemist, Stuben Glass Works

CARRIER, AUGUSTUS, B.S.(in E.E.), 20 Milwaukee Ave., W., Detroit, Mich.	Chemist, Detroit Dental Manufacturing Company
CASE, W. W., JR., Denver, Colo.	President and Manager, Denver Fire Clay Company
CASEY, CHARLES L., D.D.S., Cambridge, Ohio	President, Guernsey Earthenware Company
CERMAK, FRANK, 116 4th Ave., Schenectady, N. Y.	Foreman, Porcelain Works, General Electric Company.
CHAMBERS, A. R., 138 W. State St., Trenton, N. J.	Fire Brick Manufacturer
CHASE, JOHN ALBION, 906 S. Goodwin Ave., Urbana, Ill.	Student in Ceramics, University of Illinois
CHASE, MARCH F., B.Sc., Depue, Ill.	General Superintendent, Mineral Point Zinc Company; Greendale Plant
CHILD, J. L., Findlay, Ohio	Hancock Brick and Tile Company
CHORMANN, OTTO IRVING, Rochester, N. Y.	Chemist, The Pfaudler Company
CLAFLIN, W. N., Lancaster, O.	Lancaster Leather Board Company
CLARK, ARTHUR B., M.AR., Stanford University, California	Head Department of Graphic Arts, Leland Stanford Junior University
CLARK, JOHN, 187 Browne Ave., Flushing, N. Y.	Superintendent, New York Architectural Terra Cotta Company
CONKLING, SAMUEL O., Philadelphia, Pa.	Superintendent, Conkling-Armstrong Terra Cotta Company
COOKE, M. E., 1550 Clifton Ave., Columbus, Ohio	Studio for Archtectural Sculpture
COVAN, H. E., Cleveland, Ohio	Price Electric Pyrometer Company
COX, HERALD NEWTON, B.Sc., Woodhaven, N. Y.	Chief Chemist and Division Superintendent, Lalance and Grosjean Manufacturing Company
CRAWFORD, EDWARD ANDERSON, B.L., Klondyke, Ohio	Superintendent, Smith-Phillips China Company
CREIGHTON, ELMER E. F., B.S., E.E., Union University, Schenectady, N. Y.	Consulting Electrical Engineer, General Electric Company
CHRISTIANA, ESTAVAN F., Keyport, N. J.	Architectural Tile and Faience Company
CUTTING, J. WORCESTER, Cambridge, Mass.	Superintendent, A. H. Hews and Company, Incorporated
DALZELL, WILLIAM FREDERICK, B.A., 708 Fifth St., Moundsville, W. Va.	General Foreman, Hazel Atlas Glass Company
DANIELSON, RALPH RAYMOND, B.S.(in Cer.), Urbana, Ill.	Assistant in Ceramics, University of Illinois
DEAN, CHARLES A., CR.E., Worcester, Mass.	Ceramic Engineer, Research Laboratories, Norton Company

DEANER, ALWARD LISTER, B.S.(in Chem.),
606 E. Washington St., Bloomington, Ill.
Student in Ceramics, University of Illinois

DENMEAD, WALTER ANGUS, CR.E.,
323½ Glenwood Blvd., Schenectady, N. Y.
Assistant to Engineer of Insulation, General Electric Company

DEVOE, CHAS. H.,
Old Bridge, N. J.
Assistant Superintendent, Old Bridge Enameled Brick and Tile Company

DICKEY, FRED L.,
200 New York Life Bldg., Kansas City, Mo.
General Manager, W. S. Dickey Clay Manufacturing Company

DOBBINS, T. MONROE,
Camden, N. J.
Secretary and Treasurer, Camden Pottery Company

DORNBACH, WM. E.,
Auburn, Pa.
Superintendent, Auburn Shale Brick Company

DYER, BRAINERD, A.B., B.S.,
Cleveland, Ohio.
Head of Publicity Division, National Carbon Company

EBINGER, DAVID HUGO, M.E.,
Columbus, Ohio
Superintendent, D. A. Ebinger Sanitary Manufacturing Company

EDGAR, DAVID RAYMOND,
Metuchen, N. J.
Assistant General Manager, Edgar Brothers' Company

ELLERBECK, WM. LEON, D.D.S.,
703 Boston Bldg., Salt Lake City, Utah
Manager, Nephi Plaster and Manufacturing Company

ESKESEN, BENNET K.,
Matawan, N. J.
Superintendent, N. J. Mosaic Tile Company

EVATT, FRANK G.,
705 Fulton Bldg., Pittsburgh, Pa.
District Manager, Atlantic Terra Company

FACKT, GEO. P.,
Denver, Colo.
General Manager, Denver Terra Cotta Company

FALKENBURG, M. J., M.S.,
95 Yesler Way, Seattle, Wash.
Falkenburg & Laucks, Consulting, Analytical, Inspecting Chemists and Engineers

FARREN, MABEL C.,
303 B Iroquois Apartments, 3600 Forbes St., Pittsburgh, Pa.
Instructor in Ceramics, Carnegie Institute of Technology

FERGUSON, RICHARD D.,
1700 E St., Lincoln, Nebr.
Treasurer, Yankee Hill Brick Co.

FISHER, DOUGLAS J.,
Sayreville, N. J.
Sayre and Fisher Company

FOERSTERLING, HANS, PH.D.,
100 William St., New York, N. Y.
Second Vice President. Roessler-Hasslacher Chemical Company

FORESTER, HERBERT,
Box 37, Cleveland, Ohio
Principal, Veritas Firing System Company

FORD, BERGEN G.,
Philadelphia, Pa.
Conkling-Armstrong Terra Cotta Company

FORST, A. D., B.S.,
Trenton, N. J.
President, Robertson Art Tile Company

FORST, DANIEL PARRY, A.B.,
73 N. Clinton Ave., Trenton, N. J.
Robertson Art Tile Company

FRASER, W. B., Wilson Bldg., Dallas, Texas	President, Fraser Brick Company
FREEMAN, ALF. S., Steubenville, Ohio	Secretary-Treasurer-Manager, Freeman Fire Brick Company
FRERICHS, WM. D., 111 Broadway, New York, N. Y.	Federal Terra Cotta Company
FUHRMANN, FRANK J., 3221 California Ave., St. Louis, Mo.	Student, School of Ceramics, University City
FULLER, RALPH L., Cleveland, Ohio	Partner, Harshaw, Fuller and Goodwin Company
FULPER, W. H., Flemington, N. J..	Secretary and Treasurer, Fulper Pottery Company
FULTON, KENNETH I., B.S., CR.E., 316 E. Main St., Portland, Ind.	Citizens Gas and Oil Mining Company
GALLOWAY, WALTER B., B.S., (in Arch.), Walnut and 32nd St., Philadelphia, Pa.	President, Galloway Terra Cotta Company
GARRISON, AMOS, Pocatello, Idaho	Farmers and Traders Bank
GATES, A. W., Monmouth, Ill.	General Manager, Monmouth Mining and Manufacturing Company
GATES, MAJOR E., Terra Cotta, Ill.	Superintendent, American Terra Cotta and Ceramic Company
GATES, NEIL H., People's Gas Bldg., Chicago, Ill.	Secretary and Treasurer, American Terra Cotta and Ceramic Company
GILDARD, WARREN R., 5 Works, Ford City, Pa.	Research Chemist, Pittsburg Plate Glass Company
GLADDING, AUGUSTUS L., B.Sc., Lincoln, Calif.	Gladding, McBean and Company
GODFREY, LYDIA B., PH.B., Grand-View-on-Hudson, N. Y.	Director, Glen Tor Keramic Studio
GOLDING, CHARLES E., Rear 217 S. Warren St., Trenton, N. J.	Manager, Trenton Department of Golding Sons Company
GOOD, RALPH E., Patton, Pa.	Superintendent, Geo. S. Good Fire Brick Company
GRAINER, JOHN S., 70 Cleveland St., Battle Creek, Mich.	Foreman, A. B. Stove Company
GRANT, HENRY W., CR.E., St. Marys, Pa.	Elk Fire Brick Company
GREEN, J. L., C.E., St. Louis, Mo.	President, Laclede-Christy Clay Products Company
GREENER, G. C., E.M. (in Cer.), Boston, Mass.	Director North Bennett Street Industrial School
GREGORI, JOHN N., Chicago, Ill.	Kiln Burner, Northwestern Terra Cotta Company
GREGORY, M. E., Corning, N. Y.	Proprietor, Corning Brick, Terra Cotta and Tile Company
GRUEBY, WILLIAM H., Boston, Mass.	President, General Manager, Grueby Faience Company

GUASTAVINO, RAFAEL, JR., The Fuller Bldg., 949 Broadway, New York, N. Y.	President, The R. Guastavino Company
GUNNISS, WILLIAM HEROLD, Black Eagle Club, Great Falls, Mont.	
HAAF, GEORGE, 1501 Milton Ave., Solvay, N. Y.	General Foreman, Pass and Seymour Incorporated
HALL, HERMAN A., CR.E., East Fultonham, Ohio	Superintendent, The Kirschner Brick Company
HALL, ROBERT T., East Liverpool, Ohio	Secretary and Treasurer, Hall China Company
HAMILTON, JAMES, Trenton, N. J.	Superintendent. Ideal Pottery of Trenton Potteries Company
HAMILTON, W. L., Mt. Savage, Md.	Superintendent, Union Mining Company
HANDKE, PAUL ALBERT, 135 N. Kellogg St., Galesburg, Ill.	
HANSEN, ABEL, Fords, N. J.	Proprietor and Manager, Fords Terra Cotta and S. Works
HARDY, ISAAC ERNEST, Momence, Ill.	Superintendent, Tiffany Enameled Brick Company
HARE, ROBERT L., Fulton, Mo.	Superintendent, Fulton Fire Brick Company
HARKER, H. N., East Liverpool, Ohio	General Manager, Harker Pottery Company
HARPER, JOHN LYALL, Niagara Falls, N. Y.	Chief Engineer, Niagara Falls Hydraulic Power Company
HARRIS, CHARLES T., 824 Engineers Bldg., Cleveland, Ohio	Secretary, Hollow Building Tile Manufacturers' Association of America
HARROP, CARL B., E.M., Columbus, Ohio	Assistant Professor, Ceramic Engineering, Ohio State University
HASBURG, JOHN W., 1119 LaSalle Ave., Chicago, Ill.	President, John W. Hasburg Company, Incorporated
HASSLACHER, JACOB, 100 William St., New York, N. Y.	President, The Roessler and Hasslacher Chemical Company
HASTINGS, FRANCIS N., Hartford, Conn.	Hartford Faience Company
HAVILAND, PAUL B., 45 Barclay St., New York, N. Y.	Haviland and Company
HEILMAN, KARL JOHN, B.S., 477 E. Market St., Tiffin, Ohio	The Schaffer Engineering and Equipment Company
HELFRICH, OTIS LLOYD, CR.E., Aledo, Ill.	Continental Brick Company
HENDERSON, H. B., B.SC., 1538 N. High St., Columbus, Ohio	Superintendent, Pyrometric Cone Factory
HENRY, FRANK R., Dayton, Ohio	Manager, The Dayton Grinding Wheel Company
HILL, ERCELL C., 401 Vernon Ave., Long Island City, N.Y.	Assistant Chemist, New York Architectural Terra Cotta Company

HILL, FRED JAMES, 1005 S. Fourth St., Champaign, Ill.	Student in Ceramics, University of Illinois
HINE, HOMER H., Wellsville, Ohio	Superintendent, McLain Fire Brick Company
HIPP, RALPH T., Massillon, Ohio	
HIPP, WM. G., Massillon, Ohio	Secretary and General Manager, Massillon Stone and Fire Brick Company
HITCHINS, E. S., Olive Hill, Ky.	President, Olive Hill Fire Brick Company
HOEHN, JOHN FREMONT, 500 Square, Carlinville, Ill.	Student in Ceramics, University of Illinois
HOOD, B. MIFFLIN, A.B., Candler Bldg., Atlanta, Ga.	President, B. Mifflin Hood Brick Company
HOWAT, WALTER L., CR.E., 40th and Butler Sts., Pittsburgh, Pa.	Laboratory Assistant in Ceramics, United States Bureau of Standards
HOWE, RAYMOND MILLER, B.S., 3434 Forbes St., Pittsburgh, Pa.	Fellow in Glass, Department of Chemistry, Univ. of Pittsburgh
HUMPHREY, DWIGHT ELMER, Cleveland, Ohio	General Superintendent, Deckman-Duty Brick Company
HUNT, FRANK SUMNER, 501 E. Springfield St., Champaign, Ill.	Student in Ceramics, University of Illinois
HUTH, WALTER HENRY, B.S., 1772 Columbia Rd., Boston, Mass.	General Manager, Grueby Faience and Tile Company
IRELAND, HARLEY R., Brazil, Ind.	Assistant Secretary and Superintendent, Hydraulic-Press Brick Company
IRWIN, DEWITT D., East Liverpool, Ohio	Secretary, Potters Supply Company
JACQUART, CHARLES EDWARD, B.S., South River, N. J.	Ceramist, American Enameled Brick Company
JEFFERY, JOSEPH ARTHUR, D.D.S., Detroit, Mich.	President and General Manager, Jeffery-Dewitt Company
JENKINS, NEWELL SILL, D.D.S., 180 Meadow St., New Haven, Conn.	
JENSEN, CHARLES HENRY, 156 Greene St., Brooklyn, N. Y.	President, Empire China Works
JEPPSON, GEORGE N., Worcester, Mass.	Works Manager, Norton Company
JOHNSON, ARTHUR AUGUST VICTOR, 785 W. 73rd St., Chicago, Ill.	Draughtsman and Designer, L. E. Rodgers Eng. Company
JOHNSTON, ROBERT MARSH, M.E., Rochester, N. Y.	
JUSTICE, ITHAMAR M., Dayton, Ohio	Vice-President, Manufacturers Equipment Company
KALBFLEISCH, G. C., Tiffin, Ohio	Manager, Standard Sanitary Manufacturing Company

KANENGEISER, FRED R., Bessemer, Pa.	General Superintendent, Bessemer Limestone Company
KEEHN, CLARENCE C., B.A., Canandaigua, N. Y.	Secretary and Assistant Manager, Liske Manufacturing Company, Limited
KEELER, RUFUS B., Lincoln, Cal.	Gladding, McBean and Company
KENDRICK, J. LUCIUS S., Williamston, Mich.	
KEPLINGER, ROBERT BARR, A.B., Canton, Ohio	Assistant General Superintendent, Metropolitan Paving Brick Company
KIRK, C. J., New Castle, Pa.	President and General Manager, Universal Sanitary Manufacturing Company
KIRKPATRICK, F. A., 504 S. Goodwin St., Urbana, Ill.	Student, Ceramic Department, University of Illinois
KLEIN, ABRAHAM ALBERT, B.S., Bureau of Standards, Pittsburgh, Pa.	Petrographer, Bureau of Standards
KNOLLMAN, HARRY JOHN, CR.E., 208 High St., Perth Amboy, N. J.	Ceramic Engineer, Radium Therapy Cor., Woodbridge, N. J.
KOCH, CHARLES FREDERICK, Cincinnati, Ohio	National Sales Company
KOCH, JULIUS J., 3325 Caroline St., St. Louis, Mo.	
KOHLER, WALTER J., Kohler, Wis.	President, J. M. Kohler and Sons Company
KRAUS, CHARLES ERNEST, 350 87th St., Brooklyn, N. Y.	Refractories Engineer, H. W. Johns-Manville Company
KRICK, GEORGE M., Decatur, Ind.	General Manager, Krick, Tyndall and Company
KRIEG, HENRY F., 1229 S. 60th Ave., Cicero, Ill.	Midland Terra Cotta Company
KRIEG, WILLIAM G., 1120 Chamber of Commerce, Chicago, Ill.	President, Midland Terra Cotta Company
LAMBIE, JAMES M., B.S., Washington, Pa.	Vice-President and Assistant General Manager, Findlay Clay Pot Company
LANDERS, WILLIAM FRANKLIN, Indianapolis, Ind.	Superintendeent, U. S. Encaustic Tile Works
LARKINS, SAMUEL B., Salineville, Ohio	Superintendent, National China Company
LAUGHLIN, SAMUEL OTT, Wheeling, W. Va.	President and General Manager, Wheeling Tile Company
LAYMAN, F. E., E.M. (in Cer.), The Aberdeen, Milwaukee, Wis.	Chemist, Cutler-Hammer Company
LE PAGE, JUST, Willamina, Oregon	Head Burner, Pacific Face Brick Company
LEVINGS, GEORGE VAN B., 619 Arizona St., El Paso, Texas.	Mining Engineer

LINBARGER, SILAS CARL, 103 E. Greene St., Champaign, Ill.	Student in Ceramics, University of Illinois
LINDLEY, JACOB, Tiltonville, Ohio	Riverside Potteries Company
LIVINGSTON, JOHN B., B.S.(in Met.), 5030 Walnut St., Philadelphia, Pa.	Sales Engineer, Picher Lead Company
LLOYD, HARRY, New Salisbury, Ohio	Superintendent, Colonial Clay and Coal Company
LOCKE, FREDERICK M., Victor, N. Y.	Manufacturer of Porcelain Insulators
LONGENECKER, H. L., CR.E., Mexico, Mo.	Plant Supt., Mexico Brick and Fire Clay Company
LOOMIS, GEORGE ALLEN, CR.E., 316 N. Tenth St., Ft. Dodge, Iowa	The Vincent Clay Products Company
LOUTHAN, WM. B., East Liverpool, Ohio	Manager, Louthan Supply Company
LUCAS, H. L., Metropolitan Bldg., New York, N. Y.	Assistant Secretary, National Terra Cotta Society
LYON, JOHN BOYD, 203 S. Busey Ave., Urbana, Ill.	Student in Ceramics, University of Illinois
MCBEAN, ATHOLL, 311 Crocker Bldg., San Francisco, Cal.	Secretary, Gladding, McBean and Company
MCCANN, JAMES S., Thornton, W. Va.	Superintendent,Thornton Fire Brick Company
MCCLAVE, J. M., Camfield, Mahoning Co., Ohio	General Manager, American Fire Clay Company
MCDOUGAL, TAINE G., CR.E., Flint, Mich.	Champion Ignition Company
MCELROY, ROY HARDEN, CR.E., 1930 N. Main St., Dayton, Ohio	Ceramic Engineer, C. W. Raymond Company
MACGREGOR, JOHN ROY, 1106 Tacoma Bldg., Chicago, Ill.	Chemist, Picher Lead Company
MACKENZIE, WILLIAM G., Wilmington, Del.	Manager, Golding Sons Company, Wilmington, Delaware Department
MACMICHAEL, PAUL S., Auburn, Washington	President, Northern Clay Company
MACMICHAEL, R. F., Auburn, Washington	Assistant Manager, Northern Clay Company
MCNAUGHTON, MALCOLM, M.E., Jersey City, N. J.	Superintendent, Joseph Dixon Crucible Company
MCVAY, T. M., B.S., CR.E., 918 W. Oregon St., Urbana, Ill.	Laboratory Assistant in Ceramics, University of Illinois
MADDOCK, A. M., JR., Trenton, N. J.	Vice-President, Thomas Maddock's Sons Company
MADDOCK, HENRY E., Trenton, N. J.	With John Maddock Sons Company
MADDOCK, JOHN, Trenton, N. J.	John Maddock and Sons

MALM, ARTHUR T., CR.E., Worcester, Mass.	Factory Investigator, Research Laboratories, Norton Company
MALSCH, WERNER, 100 Williams St., New York, N. Y.	Manager, Ceramic Department, The Roessler and Hasslacher Chemical Company
MALTBY, ALFRED, Corning, N. Y.	Superintendent, Corning Brick Terra Cotta and Tile Company
MANDLE, I., Wright Bldg., St. Louis, Mo.	Secretary and Treasurer, Mandle Clay Mining Company
MANDLE, SYDNEY, Wright Bldg., St. Louis, Mo.	Assistant Treasurer, The Mandle Clay Mining Company
MANDLER, CHAS, J., B.L., LL.B., 2104 Franklin Ave., Toledo, Ohio	President, Allen Filter Company
MANOR, JNO. M., East Liverpool, Ohio	Manager, The Golding Sons Company
MASON, FORTUNATUS Q., East Liverpool, Ohio	Mason Color and Chemical Company
MAYER, WALTER STANLEY, B.S., 1520 Third Ave., New Brighton, Pa.	Assistant to Manager, Mayer China Company
MAYOR, ROBERT, Trenton, N. J.	Foreman, Monument Pottery Company
MELLOR, F. G., Wheeling, W. Va.	Wheeling Tile Company
METZNER, OTTO, Cincinnati, Ohio	Superintendent of Manufacture, Rookwood Pottery Company
MIDDLETON, JEFFERSON, 1705 Kilbourne Place N. W., Washington, D. C.	Statistician, U. S. Geological Survey
MILLER, DONALD M., 633 Monmouth St., Trenton, N. J.	Secretary, Crossley Machine Company
MILLIGAN, FRANK W., Parkersburg, W. Va.	General Manager, Electric Porcelain Company
MILLSON, WALTER C., Macomb, Ill.	Student in Ceramics, University of Illinois
MINER, HARLAN S., B.S.(in Ch.), Gloucester City ,N. J.	Chief Chemist, Welsbach Company
MONTGOMERY, ROBERT J., CR.E., 912 Dickey St., Tarentum, Pa.	Assistant, Clay Research Laboratory, Pittsburgh Plate Glass Company
MOORE, HERBERT W., Tottenville, L. I., N. Y.	Atlantic Terra Cotta Company
MOORSHEAD, THOMAS COURTNEY, Alton, Ill.	Chief Engineer, Illinois Glass Company
MORGAN, FREDERICK ARTHUR, B.S., 1106 Tacoma Bldg., Chicago, Ill.	Sales Dept., Picher Lead Company
MORRIS, GEORGE D., CR.E., Irondale, Ohio	East Ohio Sewer Pipe Company
MOSES, JAMES, Trenton, N. J.	Mercer Pottery Company
MOULTON, D. A., Ironton, Ohio.	Ceramic Engineer

MULHOLLAND, VERGIL, Darlington, Beaver Co., Pa.	Engineer, Darlington Clay Products Company
MUNSHAW, LAMBERT M., North Crystal Lake, Ill.	Ceramist, American Terra Cotta and Ceramic Company
MURRAY, GERARD A., CR.E., Mt. Savage, Md.	Union Mining Company
MYERS, CHARLES H., CR.E., 10 Third Ave., Murray, Utah	Superintendent, Murray Plant, Utah Fire Clay Company
MYERS, RALPH E., 31 Franklin Ave., East Orange, N. J.	Ceramic Engineer, Westinghouse Lamp Company
NELSON, IDRIS, A.B., 135 N. Kellogg St., Galesburg, Ill.	Chemist, Purington Paving Brick Company
NICELY, CHARLES AUGUSTUS, CR.E., Ginger, Texas	Superintendent, Fraser Brick Company
NIES, FREDERICK HAROLD, D.D.S., 859 Bay Ridge Ave.., Brooklyn, N. Y.	
ORTMAN, FRED. B., CR.E., 401 Vernon Ave., Long Island City, N. Y.	Ceramic Engineer, New York Architectural Terra Cotta Company
OUDIN, CHARLES P., 1323 Third Ave., Spokane, Wash.	Manager, American Fire Brick Company
OVERBECK, ELIZABETH G., Cambridge City, Ind.	Overbeck Pottery
OWENS, FRANCIS T., Ridgway, Pa.	Treasurer and General Manager, Ridgway Brick Company
PATERSON, ALEXANDER, PH.B.,M.A., Clearfield, Pa.	Secretary and Treasurer, Paterson Clay Products Company
PELTON, HERBERT EDWARD, A.B., E.E., 1922 Dracena Drive, Los Angeles, Cal.	Secretary and Treasurer, West Coast Tile Co., Inc.
PENFIELD, L. W., Willoughby, Ohio	Vice-President and Resident Manager, American Clay Machinery Company
PENFIELD, R. C., Willoughby, Ohio	President and General Manager, American Clay Machinery Company
PEREGRINE, CLARENCE R., 411 Washington Ave., Charlerol, Pa.	General Superintendent, Macbeth Evans Glass Company
PFEIFFER, JACOB, Akron, Ohio	Miller Rubber Company
PHILLIPS, WILLIAM L., 609 Haight Ave., Almeda, Cal.	N. Clark and Sons
PIERCE, O. W., Olean, N. Y.	Olean Tile Company
PIERCE, ROBERT H. H., B.A., Box 516 Haselwood, Pittsburgh, Pa.	Chief Chemist, Harbison-Walker Refractories Company
PITCAIRN, WILLIAMS S., 44 Murray St., New York, N. Y.	Importer of China and Earthenware
PLUSCH, HERMAN A., B.Sc., Perth Amboy, N. J.	Chief Ceramic Chemist, Atlantic Terra Cotta Company

POOLE, JOSHUA, East Liverpool, Ohio	Manager, Homer Laughlin China Company
PORTER, FRED BAKER, B.S., CH.E., Fort Worth, Texas	President, Fort Worth Laboratories
POST, MALCOLM P., Commerce, Mo.	Superintendent, Post Brothers
POSTE, EMERSON P., B.S., Elyria, Ohio	Chemical Engineer, The Elyria Enameled Products Company
POWELL, WILLIAM H., 200 W. Seventieth St., New York, N.Y.	President, Atlantic Terra Cotta Company
PRESTON, FRANCIS C., 509 Cuyahoga Bldg., Cleveland, Ohio	Vice-President and Sales Manager, Dover Fire Brick Company
PRIMLEY, WALTER S., A.B., 1120 Chamber of Commerce, Chicago, Ill.	Secretary and Treasurer, Midland Terra Cotta Company
PURINTON, BERNARD S., Wellsville, Ohio	United States Pottery Company
PYATT, FRANK E., 128 Sharon Ave., Zanesville, Ohio	
RAINEY, L. B., CR.E., 42 Sherman Ave., Mansfield, Ohio	
RAMSAY, ANDREW, Mt. Savage, Md.	The Andrew Ramsay Company
RANCKE, LOUIS N., 45 Knickerbocker Bldg., Baltimore, Md.	
RANDALL, JAMES E., Indianapolis, Ind.	Junior Editor, *Clayworker*
RANDALL, THEODORE A., Indianapolis, Ind.	Editor, *Clayworker*
RATHFON, WILLIAM OWEN, 203 N. Chicago Ave., Brazil, Ind.	
RATHJENS, GEORGE WILLIAM, B.S., C.E., St. Paul, Minn.	Superintendent, Twin City Brick Company
RAYMOND, GEORGE M., 1511 Grand Ave., Dayton, Ohio	General Manager, C. W. Raymond Company
REA, WILLIAM J., Buffalo, N. Y.	Superintendent, Buffalo Pottery Company
REED, CHAS. S., 832 W. Adams St., Chicago, Ill.	President, Chicago Retort and Fire Brick Company
REYNOLDS, PIERCE B., A.B., 433 Wyoming Ave., Kingston, Pa.	Treasurer, Dorrance Terra Cotta Company
RHEAD, FREDERICK HURTEN, Santa Barbara, Calif.	President, Rhead Pottery
RICHARDSON, ERNEST, Beaver Falls, Pa.	Vice-President and Treasurer, Ingram-Richardson Manufacturing Company
RIVERS, WILLLIAM EDWARD, Old Bridge, N. J.	Vice-President, Old Bridge Enameled Brick and Tile Company

[1]*ROBERTSON, CADMON D., 18 Summer St., Keene, N. H.	Superintendent, J. S. Taft and Company, Art Potters
ROBERTSON, FRED. H., 809 N. Alvarado St., Los Angeles, Cal.	Los Angeles Press Brick Company
ROBERTSON, HUGH SCHUYLER, 303 E. Springfield Ave., Champaign, Ill.	Student in Ceramics, University of Illinois
ROBINEAU, S., 108 Pearl St., Syracuse, N. Y.	President, Keramic Studio Publishing Company
ROBINSON, LOUIS G., M.E., Fourth and Park Avenues, Newport, Ky.	
ROCKHOLD, KENNETH EDWARD, 30 N. LaSalle St., Chicago, Ill.	L. E. Rodgers Engineering Company
RODGERS, EBEN, Alton, Ill.	Secretary and Treasurer, Alton Brick Company
ROESSLER, FRANZ, 39 High St.., Perth Amboy, N. J.	Roessler and Hasslacher Chemical Company
ROGERS, GREGORY L., 725 Santa Barbara St., Pasadena, Calif.	California Pottery Company
ROSE, ARTHUR VEAL, 11 E. Thirty-sixth St., New York, N.Y.	General Manager, Haviland and Company
RUSOFF, SAMUEL, Anderson, Ind.	National Tile Company
RYAN, JOHN J., B.S., Seguin, Texas	Secretary, Seguin Brick and Tile Company
SALISBURY, BERT E., 1810 W. Genesee St., Syracuse, N. Y.	President, Onondaga Pottery Company
SANDERS, JOHN W., Moundsville, W. Va.	Enameler, United States Stamping Company
[2]*SANT, JOHN, East Liverpool, Ohio	President, The John Sant and Sons Company
SANT, THOMAS HERBERT, East Liverpool, Ohio	Secretary - Treasurer, The John Sant and Sons Company
SAUNDERS, WILLIAM EDWARD, B.S., E.M., 1401 Arch St., Philadelphia, Pa.	Engineer, United Gas Improvement Company
SCHACHTEL, S. H., CR.E., Coffeyville, Kansas	Ludowici-Celadon Company
SCHAPPER, WALTER, 192 N. Clark St., Chicago, Ill.	Salesman, Roessler and Hasslacher Chemical Company
SCHAULIN, GEORGE MARVIN, 504 E. John St., Champaign, Ill.	Student in Ceramics, University of Illinois
SCHURECHT, HARRY GEORGE, 345 Fisk St., Pittsburgh, Pa.	
SEAVER, KENNETH, S.B., Pittsburgh, Pa.	Assistant General Sales Manager, Harbison - Walker Refractories Company
SEBRING, CHARLES L., Sebring, Ohio	General Manager, Sebring Pottery Company

[1]*Died May 20th, 1914.

[2]*Died December 3rd, 1914.

SHEERER, MARY G., Newcomb Pottery Company, New Orleans, La.	Assistant Director, Newcomb Pottery
SILVERMAN, ALEXANDER, PH.B.,A.B., M.S., Pittsburgh, Pa.	Acting Director, Department of Chemistry, University of Pittsburgh
SINCLAIR, GEORGE E., Trenton, N. J.	Secretary, Star Porcelain Company
SINCLAIR, HERBERT, Trenton, N. J.	General Manager, Star Porcelain Company
SINGER, L. P., Lincoln, Calif.	Chemist, Gladding, McBean and Company
SMITH, AMEDEE M., Portland, Oregon	President, Western Clay Manufacturing Company
SMITH, HARRY W., 314 Smith St., East Liverpool, Ohio	Representative, Roessler and Hasslacher Chemical Company
SMITH, JAMES M., New Castle, Pa.	Treasurer. Shenango Pottery Company
SMITH, NORMAN G., Brunswick, Me.	Treasurer and General Manager, Maine Feldspar Company
SMITH, PERRY A., New Brighton, Pa.	Secretary, A. F. Smith Company
SOLON, ALBERT L., Fairfax, Calif.	Manager, Arequipa Pottery
SOLON, MARC, Trenton, N. J.	General Manager and Secretary Mercer Pottery Company
SPEIR, HARRY F., Cedarville, N. J.	President, New Jersey Pulverizing Company
SPIKER, JOHN A., 811 Kearns Bldg., Salt Lake City, Utah	General Manager, United States Fire Clay Company
SPRINGE, OTTO, Galesburg, Ill.	Ceramic Engineer, Purington Paving Brick Company
SPROAT, IRA E., Washington, D. C.	Junior Ceramic Chemist, U. S. Bureau of Mines
SPURRIER, HARRY, 704 Sheridan Ave., Detroit, Mich.	Chemist, Jeffery-Dewitt Company
STAMM, JOHN, 859 Ohio Ave., E. Liverpool, Ohio	Superintendent, The Croxall Chemical and Supply Company
STANGER, FREDERICH, 520 Walnut St., Philadelphia, Pa.	Sales Manager, Enterprise White Clay Company
STANGL, MARTIN, Dundee, Ill.	Haeger Brick and Tile Company
STANLEY, WILLIAM W., PH.B., Great Barrington, Mass.	Manager, Stanley Insulating Company
STAUDT, AUGUST, Perth Amboy, N. J.	President, Perth Amboy Tile Works
STEINMAYER, R. A. J., LaSalle, Ill.	Student in Ceramics, University of Illinois
STERN, NEWTON W., 67 New Montgomery St., San Francisco, Ca.	Secretary and Treasurer, Pacific Porcelain Ware Company

STEVENS, DOUGLAS F., M.E., Cayuga, Indiana	Superintendent, Acme Brick Company
STEVENSON, WM. G., Oregon, Ill.	Secretary-Treasurer, Ohio Silica Company
STOUT, WILBER, Columbus, Ohio	Geological Survey of Ohio
STOWE, CHARLES BROWN, Cleveland, Ohio	President, National Fire Brick Company
SWALM, PHAON H., Trenton, N. J.	Assistant Superintendent, Trenton Fire Clay and Porcelain Company
TAMLYN, WALTER IRVING, E.E., 280 Van Buren St., Brooklyn, N. Y.	Assistant Engineer with Ralph D. Mershon
TATTON, JOSEPH, 206 Academy St., Trenton, N. J.	Trenton Potteries Company
TEETOR, PAUL, University of Kansas, Lawrence, Kan.	State Geological Survey
TEFFT, CHARLES FORREST, B.S. (in Cer), Ridgeway, Pa.	Ridgeway Brick Company
THOMAS, CHAUNCEY RAPELJE, Essex St., Boston, Mass.	P. F. Thomas
THOMAS, DAVID C., Wellsville, Ohio	Ceramic Chemist, U. S. Pottery Company
THOMAS, GEORGE E., St. Louis, Mo.	General Superintendent, Highlands Fire Clay Company.
THOMAS, GEORGE W., East Liverpool, Ohio	President and General Manager, The R. Thomas and Sons Company
THOMAS, JAMES RAY, B.S. (in E.E.), Crawfordsville, Ind.	Manager, Standard Brick Company
TILLOTSON, EDWIN W., JR., B.A., PH.D., Pittsburgh, Pa.	University of Pittsburgh
TIMMERMAN, WALTER F., Kansas City, Kansas	Superintendent, Western Terra Cotta Company
TONE, FRANK J., Niagara Falls, N. Y.	Works Manager, Carborundum Company
TOWNSEND, EVERETT, 344 Bellevue Ave., Trenton, N. J.	General Manager, Robertson Art Tile Company
TRAUTWEIN, J. O., 417 S. Dearborn St., Chicago, Ill.	President, Trautwein Dryer and Engineering Company
TREISCHEL, CHESTER, 127 S. Chicago Ave., Kankakee, Ill.	Student in Ceramics, University of Illinois
TRUMAN, GAIL R., 5801 Manchester Ave., St. Louis, Mo.	Ceramic Chemist, St. Louis Terra Cotta Company
TURNER, A. M., M.E., Scioto ville, Ohio	Superintendent and Treasurer, Scioto Fire Brick Company
VAN SCHOIK, ELMER HOLMES, B.S., (in Cer.), Box 166, Ottawa, Ill.	Chicago Retort and Fire Brick Company

VODREY, WILLIAM E., East Liverpool, Ohio	General Manager, Vodrey Pottery Company
VOLLKOMMER, JOSEF, Bessemer Bldg., Pittsburgh, Pa.	President and Manager, The Vitro Manufacturing Company
VOLZ, WILLIAM J., St. Louis, Mo.	Superintendent, Evens and Howard Fire Brick Company
WAGNER, FRITZ, 1000 Clybourn Ave., Chicago, Ill.	Vice-President and Treasurer, The Northwestern Terra Cotta Company
WAGNER, FRITZ, JR., B.S., 2525 Clybourn Ave., Chicago, Ill.	Assistant Superintendent, Northwestern Terra Cotta Company
WALKER, CHARLES HENRY, 400 W. 4th St., East Liverpool, Ohio	Assistant Superintendent, Homer Laughlin China Company
WALKER, F. WM., JR., B.S.(in M.E.) Beaver Falls, Pa.	Superintendent, Beaver Falls Art Tile Company
WALLACE, FRANK M., Chicago Heights, Ill.	
WANKA, F. Q., 20 W. Vine St., Stockton, Cal.	
WARD, J. W., 628 E. Main St., Latrobe, Pa.	General Superintendent, Pittsburgh High Voltage Insulator Company
WEIGEL, CHARLES, Hebron, N. Dak.	President, Hebron Fire and Pressed Brick Company
WELLS, HARRY B., Canton, Ohio	Superintendent, Belden Brick Company
WHEAT, HOWARD I., 987 Sterling Place, Brooklyn, N. Y.	Vice-President, New York and New Jersey Brick Company
WHITAKER, FRED. A., Keasbey, N. J.	Superintendent, German-American Stoneware Works, Plant No. 1
WHITELAW, JAMES CAMERON, 212 Daniel St., Champaign, Ill.	Student in Ceramics, University of Illinois
WHITFORD, WILLIAM GARRISON, PH.B. (in Cer.), Chicago, Ill.	Instructor in Design and Ceramic Art, University of Chicago
WHITMER, J. D., CR.E., 9 Ball St., Zanesville, Ohio	American Encaustic Tile Company
WIGFIELD, CLAUDE LAWRENCE, 205 E. 2nd St., Elyria, Ohio	Enameler, Enamel Pipe and Engineering Company
WILDER, THOMAS MILTON, Ravinia, Ill.	Proprietor, Wildwood Shop
WILL, OTTO W., Perth Amboy, N. J.	Superintendent, Color Department, Roessler and Hasslacher Chemical Company
WILLIAMS, ARTHUR E., Urbana, Ill.	Ceramic Department, University of Illinois
WILLIAMS, IRA A., M.SC., Corvalis, Oregon	Professor Ceramics, Oregon School of Mines, Ceramist, State Bureau Mines and Geology
WILSON, GEORGE P., Steubenville, Ohio	

WILSON, HEWITT, CR.E., Auburn, Washington	Ceramic Chemist, Northern Clay Company
WOODS, WILLIAM J., A.B., Lewistown, Pa.	Assistant General Manager, Pennsylvania Pulverizing Company
WORTH, S. HARRY, 706 Franklin Bank Bldg., Philadelphia, Pa.	President, Pennsylvania Feldspar Company
YATES, ALFRED, Shawmut, Elk County, Pa.	General Manager, Shawmut Paving Brick Company
YEARSLEY, HOWARD S., 304 State St., Camden, N. J.	Manager, Electrical Porcelain and Manufacturing Company
YOUNG, GEORGE F., Zanesville, Ohio	Manager, Roseville Pottery Company
YOWELL, JOHN BENNETT, Falls Creek, Pa.	Ridgeway Brick Company
ZOPFI, ALBERT S., Toledo, Ohio	Secretary and Treasurer, Buckeye Clay Pot Company

DETROIT, MICHIGAN, February 15, 1915.

To the Members of the American Ceramic Society:

The Board of Trustees takes pleasure in submitting the following report of the Society's activities for the fiscal year ending February 1st, 1915:

MEMBERSHIP

The growth of the Society has been slow this year. A total gain in membership of 17 seems altogether too little for an organization representing an industry which produces over 180 millions dollars worth of output, and in which not less than 15,000 owners, managers, superintendents, engineers, chemists and technical men are engaged, from which classes our membership is chiefly recruited. The enormous army of workers in the clay and allied industries is not considered because in the nature of the case it is not from their ranks in any large degree that our members come.

The following table gives an analysis of the year's growth:

		TOTALS
BROUGHT FORWARD FEBRUARY 24TH, 1914:		
Honorary members	4	
Contributing members	4	
Active members, resident	57	
Active members, foreign	10	
Associate members, resident	350	
Associate members, foreign	41	466
ACCESSIONS BY ELECTION DURING FISCAL YEAR:		
Active members, resident	5	
Active members, foreign	1	
Associate members, resident	57	
Associate members, foreign	7	70
LOSSES DURING THE FISCAL YEAR:		
By death	5	
By resignation	8	
By transfer or promotion	9	
Dropped for non-payment of dues	31	53
STATUS FEBRUARY 1ST, 1915:		
Honorary members	4	
Contributing members	2	
Active members, resident	61	
Active members, foreign	10	
Associate members, resident	360	
Associate members, foreign	46	483
Net gain		17

The significant feature in this table is the loss of thirty-nine persons from our rolls from what is certain to be, at bottom, loss of interest. Deaths and changes of grade are inevitable, but resignations and dropping from the rolls for failure to pay the dues means that the Society is not filling its function properly or that people join it without proper consideration, and find after joining that they are not interested in our work and therefore drop out. The number of persons joining is satisfactory, and constitutes as large a number as we can comfortably assimilate and bring into active and appreciative relations.

The relation between the growth of the Society this year and for some years preceding is shown in the following table:

	ACTIVE	ASSOCIATE	TOTAL	INCREASE
1906	35	149	185	..
1907	41	188	231	46
1908	47	207	256	25
1909	50	251	303	47
1910	54	284	340	37
1911	54	325	381	41
1912	63	360	425	44
1913	65	384	456	31
1914	67	391	466	10
1915	71	406	483	17

Plotting this data in curve form it is easily seen that from 1906 to 1912 the increase ascends with uniform gradient, but that during the last three years we have fallen about 65 members behind the projected continuation of the 1906-1912 line.

The net deductions from a study of these facts are two:

1st, We should, one and all, make a much stronger effort to keep our members interested when we get them. This means personal interest, a kind reception at meetings, correspondence between meetings, exchange of data, etc.

2nd, We should use discrimination as well as zeal in securing new members. A careful explanation in the beginning as to what we stand for and what the implied obligations of membership are, might conceivably make our accessions a little slower but our net gain greater.

FINANCIAL STATEMENT

Receipts

Brought forward from preceding year	$ 759.79	$ 759.79
Receipts from Dues for 1914:		
Active members	450.00	
Associate members	1,715.00	
Contributing members	50.00	
Collections on arrearages	97.97	
Payments made in advance	40.52	2,353.49
Receipts from Initiation Fees:		
From active members	40.00	
From associate members	220.00	260.00
Receipts from Sale of Publications:		
From Transactions	704.83	
From Branner Bibliography	23.13	
From Seger's Collected Writings	67.50	
From cloth binding	149.75	
From Reprints	165.94	1,111.15
Receipts, miscellaneous	1.25	1.25
Total		$4,485.68

Disbursements

Publication of Volume XVI:		
Stenographic report	$ 150.00	
Drawings, illustration and engraving	356.20	
Printing, binding and casing	1,183.15	
Editor's salary	600.00	$2,289.35
Paid for Seger's Collected Writings	41.79	
Paid for reprints (sold to authors)	128.25	170,04
Paid for Administration:		
Salary for assistant secretary	300.00	
Extra clerk hire	41.67	
Postage, stationery and supplies	153.06	
Insurance on volumes	14.00	
Telegraph and telephone	9.27	
Transportation of volumes by express and mail	130.74	
Binding and casing early volumes	12.75	
Expenses at convention	49.95	
Boxing, labeling, moving publications from University to Fireproof Storage Co	45.05	756.49
Total		$3,215.88
Cash balance in bank		1,269.80
Total		$4,485.68

Assets

Cash in bank		$1,269.80
Accounts payable:		
Dues and fees due but not collected	$ 292.90	
Publications sold, but not paid for	177.59	
Reprints ordered but not paid for	19.95	490.44
Books on hand:		
2,079 Volumes of Transactions @ $3.70	7,692.30	7,692.30
Stock, stationery, fixtures, etc., (estimate)	50.00	50.00
Total		$9,502.54

Liabilities

There are no liabilities other than a few minor accounts for supplies, bills for which have not been rendered.

The foregoing analysis, upon comparison with last year's, reveals the fact that the year has not been so healthy as our increased bank balance would at first sight imply.

The comparison shows that the receipts for 1914 and 1915 respectively were:

Receipts

	1913–1914	1914–1915
Dues	$2,415.65	$2,353.49
Fees	305.00	260.00
Sales	1,456.41	1,111.15
Miscellaneous	4.03	1.25
	$4,181.09	$3,725.89
Expenditures		
Volumes	$2,658.49	$2,289.35
Other literature	161.50	170.04
Administration	851.17	756.49
	$3,671.16	$3,215.88
Balances		
	$ 509.93	$ 510.01
Brought forward from preceding year	249.86	759.79
Carried forward to succeeding year	$ 759.79	$1,269.80

In short, our income decreased, in every department, by a total of $455.20, but we made a corresponding economy in expenses of almost exactly the same amount ($455.26), so that while each year shows that our affairs were handled at a net gain of about $510.00, and our cash balance in two years has gone up over $1,020.00, it has been by careful management and not by growth and increasing activity of the organization.

The logic of this analysis is the same as that of the membership table. It calls for more interest, more personal responsibility, on the part of the whole membership. While we are in a sound financial condition, we have a decreasing revenue, and that condition cannot go on long without disastrous results.

Publications

Volume XVI. Volume XVI was gotten out in Columbus by Editor Arthur S. Watts, and distributed in the early fall. It contains 58 articles, covering 553 pages, and with 52 pages of announcements and business matter and 5 pages of index, makes a very creditable volume of 611 pages. A scrutiny of the list of titles shows a number of new fields of study not before treated in our literature, and the author list also shows a number of new names whose entrance into our field augurs well for the future.

Supply of Publications on hand: A careful physical inventory was made this year, in connection with the removal of the volumes from Lord Hall, Ohio State University, to the Fire Proof Storage and Ware House Company, of Columbus. At this time, they were carefully labeled, boxed and put in the best possible condition.

The following table gives the facts:

NUMBER OF VOLUME	NUMBER REMAINING ON HAND FEBRUARY 1915	RECEIVED SINCE	DISPOSED OF BY SALE	EXCHANGES	IN STOCK FEBRUARY 1915 BY PREVIOUS RECORD	IN STOCK FEBRUARY 1915 BY ACTUAL COUNT
I	156		3		153	152
II	117		7		110	112
III	153		2		151	149
IV	127		2		125	125
V	94		3		91	91
VI	123		3		120	119
VII	124		2		122	128
VIII	118		6		112	110
IX	79		5		74	74
X	108		4		104	103
XI	128		2		126	139
XII	106		5		101	94
XIII	205		9		196	196
XIV	79		14		63	109
XV	184		37		146	146
XVI		753	495	26	232	232
Branner Bibliography	776		11	5	760	760
Total stock on hand						2,839

Summer Session

Under the management of a committee of five, of which Mr. A. F. Greaves-Walker, of Toronto, Canada, was chairman, a very pleasant and effective summer meeting was held in Southern Canada. The points visited were in the Toronto district. About 25 persons attended. A detailed report, with views taken enroute, has been filed by the committee and placed on record in the Society's minutes.

Index vs. Prospectus

The need of a thorough subject and author index of the volumes now printed as well as those to follow, has been discussed by the Society on a number of occasions. Steps have been taken at one time to provide such an index, but not fully carried out. The index of the volumes beginning with No. X are fairly complete and satisfactory, each for its own volume, but they do not fill the need of the general index. The amount of matter contained in the first 16 volumes is not sufficient by itself to make a volume of desirable size, but by the 20th volume, it would. The Board of Trustees thinks that an index should be started at once, basing it upon the indices of Volumes 10-16, and going over Volumes 1-9, and adding all subsequent indices as they are prepared. Such an index would necessarily be kept in card form till ready for printing, and will therefore be available for use only at the Secretary's office.

To bridge the gap for the next four years, the Board has decided to print a prospectus, containing a complete list of the titles of all papers printed thus far, by volumes. Such a list falls far short of being an index, but it will very materially shorten the time required to go over the Transactions in search of any particular topic. It will also form an effective advertisement and reply circular for use in the office of the Secretary. Such a prospectus will amount to about 40 pages, and will be furnished free to every member.

The New Amendments

The legislation regarding Student Branches of the Society in technological schools supporting departments of Ceramics, and local sections of the Society, to be established wherever enough of our membership resides in one locality to make frequent meetings possible, has been before the Society for a year, and it is hoped that the ballot will be authorized at this meeting. Since no opposition has been voiced, it is assumed that the amendments will carry when the ballot is taken. The Board of Trustees looks forward to most useful and important results from these movements. They should add not only to our membership, but to our productive scholarship in the science. Applications are on file from the Ohio State University

Ceramic Society and the Beaver Ceramic Society to be made into the Ohio State University Student Branch and the Beaver Section respectively, so soon as the necessary legislation has been put through. The amendments will be printed in the Rules in Vol. XVII if adopted at the time of publication.

Conclusion

In spite of the declining revenue, and the decrease in rate of net growth discussed in the earlier portion of this report, the Board believes that the year has been a good one and that the usefulness of the Society has never been greater or its future more assured. Only in proportion as its members put their vigor and their thought into it, can this be realized. The Board believes that this will not be lacking.

FOR THE BOARD OF TRUSTEES,

By Edward Orton, Jr., *Secretary*

RULES OF THE SOCIETY

[Revised 1915]

I

OBJECTS

The objects of the American Ceramic Society are to promote the arts and sciences connected with ceramics by means of meetings for the reading and discussion of professional papers, the publication of professional literature, and for social intercourse.

II

MEMBERSHIP

The Society shall consist of Honorary Members, Active Members, Associate Members and Contributing Members.

Honorary members must be persons of acknowledged professional eminence, whom the Society wishes to honor in recognition of their achievements in ceramic science or art. Their number shall at no time exceed two percent of the combined active and associate membership.

Active members must be persons competent to fill responsible positions in ceramics. Only Associate Members shall be eligible to election as Active Members, and such election shall occur only in recognition of attainments in the field of ceramics, and interest in the Society, as evidenced by papers or discussions contributed to its meetings.

Associate Members must be persons interested in ceramics or allied arts.

Contributing Members must be persons, firms, or corporations who, being interested in the Society, make such financial contributions for its support as are prescribed in Section 3.

Honorary Members shall be nominated for election by at least five active members, and approved by the Board of Trustees. Their nomination shall be placed before the Society at an annual meeting, and to be elected they must receive the affirmative vote of at least 90 percent of those voting, by letter ballot, at the next succeeding annual meeting.

To be promoted to active membership, Associate Members must be nominated in writing by an Active Member, and must be seconded by not less than two other Active Members, and must be approved by the Board of Trustees. Their nomination shall be accompanied by a statement of their professional qualifications and a list of their

publications, if any. Their nominations, when approved by the Board of Trustees, shall be placed before the Society at an annual meeting, and to be elected they must receive the affirmative vote of not less than 75 percent of those voting, by letter ballot, at the next succeeding annual meeting.

A candidate for Associate Membership must make application upon a form, prepared by the Board of Trustees, which shall contain a written statement of the age and professional experience of the candidate, and a pledge to conform to the laws, rules and requirements of the Society. Such applications must be endorsed by two Active Members of the Society as sponsors, and must be approved by the Board of Trustees. The Board may act by letter ballot upon such application at any time, after which an approved candidate may be enrolled on the proper list of the Society upon payment of the fees and dues prescribed in Section 3.

Contributing Members shall be nominated by an Active Member, and approved by the Board of Trustees, and may be enrolled on the proper list of the Society at any time upon payment of the dues prescribed in Section 3.

All Honorary Members, Active Members, Associate Members, and Contributing Members shall be equally entitled to the privileges of membership, except that only Active Members shall be entitled to vote and hold office. The roster of each grade of membership shall be printed separately, in at least one publication issued by the Society annually. Any person may be expelled from any grade of the membership of the Society if charges signed by five or more active members are filed against him, and a majority of the Board of Trustees examines into said charges and sustains them. Such person, however, shall first be notified of the charges against him, and be given a reasonable time to appear before the Board of Trustees, or present a written defense, before final action is taken by the Board of Trustees.

III

DUES

Honorary Members shall be exempt from all fees or dues.

The initiation fee of Active Members shall be ten dollars, and if not paid within three months after the date of their election, the latter shall be null and void. The annual dues for Active Members shall be fixed by the Board of Trustees, and shall not exceed ten dollars.

The initiation fee of Associate Members shall be five dollars, and their annual dues shall be fixed by the Board of Trustees, but shall not exceed five dollars. The privileges of Associate Membership after election shall begin upon payment of the initiation fees, and dues for the first year.

Contributing Members shall pay no initiation fee into the Society. Their annual dues shall be fixed by the Board of Trustees, but shall not exceed twenty-five dollars. The privileges of membership shall begin upon payment of the annual dues.

Any Active Member or Associate Member in arrears for over one year may be suspended from membership by the Board of Trustees, until such arrears are paid, and in event of continued dereliction, may be dropped from the rolls. Active Members in arrears are not eligible to vote. The annual dues of Active and Associate Members are payable within three months succeeding date of annual meeting.

IV

OFFICERS

The affairs of the Society shall be managed by a Board of Trustees, consisting of a President, Vice-President, Secretary, Treasurer and three Trustees, who shall be elected from the Active Members at the annual meeting, and hold office until their successors are elected and installed.

The President, Vice-President, Secretary and Treasurer shall be elected for one year, and the Trustees for three years; and no President, Vice-President, or Trustee shall be eligible for immediate re-election to the same office.

The duties of all officers shall be such as usually pertain to their offices, or may be delegated to them by the Board of Trustees or the Society; and the Board of Trustees may, at its discretion, require bonds to be furnished by the Treasurer.

Vacancies in any office shall be filled by appointment by the Board of Trustees, but the new incumbent shall not thereby be rendered ineligible to re-election at the next annual meeting to the same office. On the failure of any officer to execute his duties within a reasonable time, the Board of Trustees, after duly warning such officer, may declare the office vacant, and appoint a new incumbent.

A majority of the Board of Trustees shall constitute a quorum, but the Board of Trustees shall be permitted to carry on such business as it may desire by letter.

V

ELECTIONS

At the annual meeting, a Nominating Committee of five Active Members, not officers of the Society, shall be appointed, and this committee shall send the names of the nominees to the Secretary at least sixty days before the annual meeting who shall immediately forward the same to the Active Members. Any other five Active

Members may act as a self-constituted Nominating Committee, and also present the names of any nominees to the Secretary, provided it is done at least thirty days before the annual meeting. The names of all nominees provided their assent has been obtained, shall be placed on the ballot without distinction as to nomination by the regular or self-constituted Nominating Committee, and shall be mailed to every member, not in arrears, at least twenty days before the annual meeting. The ballot shall be enclosed in an inner blank envelope, and the outer envelope shall be endorsed by the voter, and mailed to the Secretary. The blank envelopes shall be opened by three scrutineers appointed by the President, who will report the result of the election at the last session of the annual meeting. A plurality of votes cast shall elect.

VI

MEETINGS

The annual meeting shall take place on the first Monday in February, or as soon thereafter as can be conveniently arranged, at such place as the Board of Trustees may decide, at which time a report shall be made by the Board of Trustees, Treasurer and scrutineers of election, and the accounts of the Treasurer shall be audited by a committee of three, appointed by the President. Ten Active Members shall constitute a quorum at any regular meeting, and a majority shall rule unless otherwise specified.

The order of business at the annual meeting shall be:

1. President's address.
2. Reading of minutes of last meeting.
3. Reports of the Board of Trustees and Treasurer.
4. Appointment of committees.
5. Old business.
6. New business.
7. Reading of papers.
8. Announcement of election of officers, Honorary and Active Members.
9. Installation of officers and new members.
10. Adjournment.

Other meetings may be held at such time and places during the year as the Board of Trustees may decide, but at least twenty days' notice shall be given of any meeting.

The President shall appoint at the annual meeting a committee of five, to be known as the Summer Meeting Committee, whose duty it shall be to arrange for a summer excursion meeting at some suitable point. The expenses of the Summer Meeting Committee in arranging the program of visits and for printing, rooms and facilities for meetings, shall be borne by the Society.

VII
PUBLICATIONS

The Board of Trustees shall employ, at suitable compensation, an Active Member of the Society as Editor of its publications. The Editor, together with the Secretary and Treasurer, shall constitute a Publication Committee. The Publication Committee shall provide for the publication of an annual volume, entitled "Transactions of the American Ceramic Society." This volume shall contain a list of the officers, a list of members of the Society, classified into grades, a list of the ex-Presidents, the dates and location of meetings, the annual report of the Board of Trustees and Treasurer, the list of prices of the publications of the Society, the rules of the Society, and any other matter pertaining to the business administration of the Society that the Publication Committee may think proper. It shall also contain such of the papers and discussions thereon as the Publication Committee may consider desirable, and each volume shall contain a list of the papers and discussions and an index. The volume shall be six inches wide by nine inches long, and part of the issue shall be bound in paper covers and part in cloth binding. The quality of the paper, the kind of type, the illustrations, and all other mechanical details of the printing and publishing of the books or reprints shall be in the hands of the Publication Committee, subject to the control of the Board of Trustees.

The acts and policies of the Publication Committee shall at all times be subject to the examination and approval of the Board of Trustees, but the Board shall be bound by contracts entered into by the Publication Committee in the name of the Society. The Publication Committee shall have full power and authority to decide what papers and discussions to publish, which discussions shall be germane to the subject matter, and in what order they shall be published, and in what manner and to what extent they shall be illustrated. In event that the Board of Trustees shall undertake the publication of some other matter or book than the Transactions, the Publication Committee shall act in the same capacity for that publication as in the publication of the annual volume of the Transactions.

One copy of the paper-bound edition of the Transactions shall be sent prepaid to each member of the Society not in arrears. Members desiring cloth-bound copies will be furnished them in place of the paper-bound copy at an increased cost for the binding. No member shall be furnished more than one copy of the Transactions free for any single year. Members cannot purchase extra copies of the Transactions at less than the current commercial rates. A member shall be permitted to purchase one complete file of the publications of the Society at less than the current commercial rate, the amount to be fixed by the Publication Committee and called the Member's rate.

The Secretary shall have the custody of all publications of the Society, shall keep them safely stored and insured, and shall sell these volumes to the public at prices which shall be fixed by the Publication Committee for each new volume as issued. The Publication Committee shall also, from time to time, fix the price of the old volumes remaining unsold, and shall have authority to refuse to sell the old volumes of the Transactions except in sets, at such time as the quantity remaining of any number becomes so small, as in their judgment to warrant such action.

The Editor shall request the author of each article appearing in the Transactions of the Society to fill out and sign, within a definite time limit, a blank form, specifying the number of reprints of said article, if any, which he desires. This form shall contain a table from which can be computed the approximate cost at which any reprints will be furnished. In event that the expense of furnishing the desired number of reprints is large, the Publication Committee may require the author to pay in advance for part or all of the cost involved before the publication of the reprints is begun. On receipt of such signed order within the time limit set, the Editor shall cause to have printed the desired number of copies. If the author makes no reply, or replies after the time limit has expired, then the Society will not be responsible for the publication of any reprints of the article in question, except at the usual market price for the printing of new matter.

No one shall have the right to demand the publication of an article independent of the discussion which accompanied it, and no one having taken part in a discussion upon an article shall be entitled to order reprints of the discussion separately and apart from the article itself.

The Society is not, as a body, responsible for the statements of facts or opinions expressed by individuals in its publications.

VIII

PARLIAMENTARY STANDARD

Roberts "Rules of Order" shall be the parliamentary standard on all points not covered by these rules.

IX

AMENDMENTS

To amend these rules, the amendment must be presented, in writing, at the annual meeting of the Society, and must be printed on the ballot for officers and sent out not less than twenty days in advance of the next annual meeting, and if the said letter ballot shows an affirmative vote of not less than two-thirds of the total vote cast, then the same shall be declared carried.

X

LOCAL SECTIONS

Designation. Local Sections, each carrying some distinguishing title prefixed to the words "Section of the American Ceramic Society," may be authorized by the Society.

Purpose. The purposes of such sections shall be to strengthen and extend the work of the Society as defined in Section I of its Rules, by more frequent meetings in local centers than are possible to the Society as a whole, and by bringing the benefits of the work to persons who would not otherwise be reached.

Granting of Charters. Appliaction for permission to form a local section must be in writing and signed by not less than ten members of the Society in good standing, residing in the general locality where the section is to be formed, of whom one at least shall be an Active member. To be considered at any given meeting, an application must be filed with the secretary at least 30 days prior to the date of the meeting, and notice that the application is pending must appear in the program of the meeting. To be granted, the application must receive the affirmative vote of two-thirds of those present. In event of affirmative action, the Society will issue a charter to the applicants, authorizing them to form a section under the name proposed. Charters for local sections may be temporarily suspended by the Board of Trustees for cause, but no charter can be permanently rescinded, except by vote of two-thirds of those present at a regular meeting of the Society after due publication in the program of the meeting that the matter is pending.

Legislative Powers. Local sections shall have power to make their own rules and by-laws, except that they shall not pass any rule or by-law which is in conflict with the Rules of the Society.

Officers. The Officers of local sections shall be a Chairman, a Secretary and a Councilor, and such others as the Section may prescribe. The duties of the Chairman and Secretary shall be such as usually pertain to those offices. The Councilor must be an Active member of the Society, and it shall be his duty to advise the Section in all matters pertaining to its relations with the Society, and to make an annual report to the Society regarding the work and status of the Section. The names of the Chairman, Secretary and Councilor of each Section shall appear in the roster of the Society in the Annual Volume of the Transactions of the Society.

Eligibility. Only members of the Society shall be eligible to full participation in the work of local Sections, but Sections may provide in their by-laws for a limited participation in their work by persons not members of the Socety, when in their opinion the purposes of

the Society will be subserved by such a course, provided always that such persons shall not vote or hold office in the Section.

Finances. Local Sections shall have power to fix their own dues or assessments, such dues or assessments being in addition to and independent of the regular dues and assessments of the Society upon its members. No Section shall have authority to incur debt in the name of the Society or for which the Society may become liable.

XI

STUDENT BRANCHES

Designation. Student Branches, each carrying some distinguishing title prefixed to the words "Student Branch of the American Ceramic Society," may be established in Institutions in which regular courses of instruction in Ceramics are maintained.

Purpose. The purposes of such Student Branches shall be to strengthen and extend the work of the Society, as defined in Section I of the Rules, by enlisting the interest and support of students of Ceramics while still in schools, and by stimulating the spirit of ceramic research among them.

Granting of Charters. Application to form a Student Branch in any institution must be in writing, and signed by not less than five regularly enrolled students in good standing and endorsed by two or more members of the Society. The application must be filed and acted upon as provided for Local Sections in Section X, and may be suspended or revoked for cause in the same manner.

Legislative Powers. Student Branches shall have power to make their own rules and by-laws, except that they shall not pass any rule or by-law in conflict with the Rules of the Society.

Officers. The officers of Student Branches shall be a Chairman, a Secretary, a Councilor, and such others as the Student Branch may prescribe. The Chairman and Secretary shall be elected by the Student Branch, and their duties shall be such as usually pertain to these offices. The Councilor shall be an active member of the Society, appointed by the Board of Trustees to act in this capacity to the Student Branch. The duties of the Councilor shall be to advise the Student Branch in all matters pertaining to its relations to the Society and to make an annual report to the Society regarding the work and status of the Student Branch. The names of the Chairman, Secretary and Councilor for each Student Branch shall appear in the Roster of the Society in the Annual Volume of the Transactions.

Eligibility. Membership in a Student Branch shall be limited to the instructional force and regularly enrolled students of schools in which branches are located, subject to the rules of the school concerned governing outside activities of students.

Finances. Student Branches shall have power to fix their own dues and assessments, and as such shall pay no dues or initiation fees to the Society. No Student Branch shall have authority to incur debt in the name of the Society or for which the Society may become liable.

Relation to Parent Society. Members of a Student Branch as such shall pay no dues or initiation fees to the Society, but upon depositing a certificate of good standing from their Secretary may purchase from the Society its Transactions at the same rate as Associate members of the Society. This privilege shall cease when the student's connection with the school ceases, but members of a Student's Branch upon leaving school may at once become associate members of the Society, by depositing their certificates, making the proper application, and paying the regular initiation fee.

PUBLICATIONS

The following is a list of the volumes published by the Society and the prices at which they are for sale to the general public:

Description of volume.			Bound in paper.	Bound in cloth.
Vol. I.	1899,	110 pages.....	$4.00	$4.75
Vol. II.	1900,	278 pages.....	4.00	4.75
Vol. III.	1901,	238 pages.....	4.00	4.75
Vol. IV.	1902,	300 pages.....	4.00	4.75
Vol. V.	1903,	420 pages.....	5.00	5.75
Vol. VI.	1904,	278 pages.....	4.00	4.75
Vol. VII.	1905,	454 pages.....	4.00	4.75
Vol. VIII.	1906,	411 pages.....	4.00	4.75
Vol. IX.	1907,	808 pages.....	5.00	5.75
Vol. X.	1908,	582 pages.....	5.00	5.75
Vol. XI.	1909,	632 pages.....	5.50	6.25
Vol. XII.	1910,	882 pages.....	5.50	6.25
Vol. XIII.	1911,	837 pages.....	5.50	6.25
Vol. XIV.	1912,	888 pages.....	5.50	6.25
Vol. XV.	1913,	747 pages.....	5.50	6.25
Vol. XVI.	1914,	611 pages.....	5.50	6.25
Vol. XVII.	1915,	pages.....	*....	6.25
Complete Set			$76.00	$94.25

* Volume XVII and all following Volumes will be bound in cloth only.

The Board of Trustees established in the beginning a differential between members of the Society and others, in the matter of prices to be paid for copies of the Proceedings. This differential has been changed from time to time as volumes have grown scarcer and sales increased. The present arrangement, which will stand until March 1, 1915, allows a straight discount of 40 percent to members in good standing. Members in arrears are not furnished copies of the volume for the current year, nor allowed the discount for the older publication. Members are also not permitted to purchase more than one full set of the publications at members' rates. The care and sale of the Publications has been transferred to the Publication Committee, which reserves the right to change the discount from time to time on any one volume or on all, as may be necessary.

The number of copies of the earlier volumes is not large, and members are advised to procure full sets as soon as possible. The prices will never be less and will certainly rise as time goes on.

In addition to the above volumes of the Transactions, the Society has also published the following books, which will be sold *net* at the prices listed to the public and members alike:

The Collected Writings of Dr. Hermann August Seger, Volume I. Contains (*a*) Treatises of a General Scientific Nature. (*b*) Essays Relating to Brick and Terra Cotta, Earthenware and Stoneware, and Refractory Wares. Pages, 552. Bound in cloth..... $7.50

The Collected Writings of Dr. Hermann August Seger, Volume II. (*b*) Essays on White Ware and Porcelain. (*c*) Travels, Letters and Polemics. (*d*) Uncompleted Works and Extracts from the Archives of the Royal Porcelain Factory. Pages, 605. Bound in cloth..... 7.50

A Bibliography of Clays and the Ceramic Arts, by Dr. John C. Branner, 1906, 451 pages. Bound in cloth. Contains 6027 titles of works on Ceramic subjects..... 2.00

The above publications will be shipped at the consignee's expense, by express, to any address on receipt of the price. All checks or money orders should be made payable to the American Ceramic Society, and not to the Secretary or the Treasurer.

EDWARD ORTON, JR.,

Columbus, Ohio. *Secretary.*

IN MEMORIAM

CHARLES GLENVILLE BLAKE, M. E.

CADMON D. ROBERTSON

JOHN SANT

PAPERS AND DISCUSSIONS

PRESIDENTIAL ADDRESS

OUR INDUSTRY AND THE FOREIGN TRADE

BY CULLEN W. PARMELEE

In a manuscript which is supposed to have been written at about 1688, and which is deposited in the Bodleian Library at Oxford, there is found this statement:

"I have erected a pottery at Burlington for white and chiney ware, a great quantity of ye value of £1200 have been already made and vended in ye country, neighboring colonies and ye Islands of Barbadoes and Jamaica where they are in great request."

From this ancient record we learn of the beginning of the whiteware industry in this country and also of the beginning of our export trade in clay products.

In 1766, Josiah Wedgewood who had received some samples of clay from this country wrote to a friend that "They (the colonies) have every material there, equal if not superior to our own for carrying on the manufacture * * * and these emigrations (of potters to the colonies) make us very uneasy for our trade and Posterity."

The course of events during the past six months, which has wrought such a tremendous change among so many leading industrial nations of the world has brought forth commercial problems which quicken the imagination and stir the pulse of the nation. There is scarcely a newspaper or magazine which does not reflect that uneasiness which Josiah Wedgewood felt for "trade and Posterity." Such headlines as: "World War for Trade," "Trade Opportunity for United States" "War and American Export" meet our eyes, as we glance through the pages of our most conservative journals.

It has seemed to me, therefore, that we may do as our foreign friends are doing, that is, consider our industry in its relations to the import and export trade of our country. I cannot presume to do more than present to you the facts regarding our foreign commerce, for I would be rash indeed to attempt to

prophesy and will leave that to those who have the courage of convictions based upon a fuller knowledge of the intricacies of foreign trade.

In order not to weary you unnecessarily, I have chosen to present the facts, which I have gleaned, in the form of charts rather than by long lists of figures.

Figure 1 shows by curves the relation between the increase of the population of the United States during the period 1905-1912 and the production of clay wares for the same period.

Population increased 15 percent.

Production increased 21 percent.

Imports decreased 14.0 percent.

Exports increased 16.8 percent.

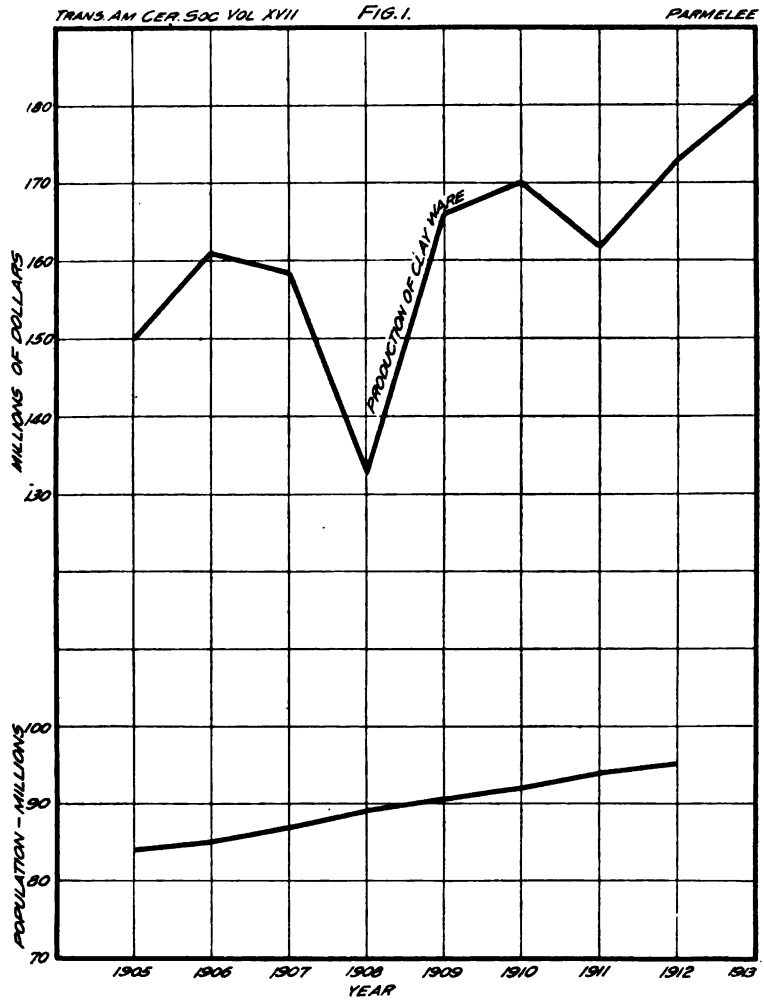
Looking at this from another point of view, the increase in the value of products was approximately 32,000,000 dollars, while our exports increased 3,000,000 dollars, which gave a net increase of 29,000,000.

Population increased 15 percent, domestic consumption increased 18 percent.

In compiling this data, we have had in mind particularly the trade between the warring countries of Europe: namely, Austria-Hungary, Belgium, France, Germany and the United Kingdom of Great Britain and Ireland, on one hand and the United States on the other; also the trade relations of these several countries with South America.

Imports of Clays by the United States. (Figure 2.) Great Britain is by far the largest shipper, and the one item of kaolins received from that country far exceeds the total value of all other clays from the several countries named. Austria sends us some and Germany a smaller quantity.

Second in value to the kaolins is the total of the classification known as "other clays," of which Great Britain is the chief shipper,—value of all clays, 2,025,602 dollars. Of this latter class, France is the next most important shipper, and the other countries follow with smaller amounts. Under the classification of "crucible clays" Germany stands first and provides a great quantity—value of all clays 228,271 dollars.


TRANS. AM CER. SOC VOL XVII
FIG. I.
PARMELEE
MILLIONS OF DOLLARS
180
170
160
150
140
130
PRODUCTION OF CLAY WARE
POPULATION - MILLIONS
100
90
80
70
1905
1906
1907
1908
1909
1910
1911
1912
1913
YEAR

The cessation of importations by the United States wholly or in part from Austria-Hungary and Germany has been promptly felt in this country. This has led to energetic measures being taken by American importers to find substitutes among our domestic clays.

Exports of Clays by the United States. (Figure 3.) Much surprise was occasioned the writer upon discovering among the statistics of Commerce and Navigation, Dept. of Commerce, for 1913, (U. S. Govt. Document) that we exported clays during that year to Germany, our chief customer, to the value of 96,858 dollars. Belgium comes second with a consumption of 23,503 dollars, and Great Britain third with 20,161 dollars. Small quantities of fire clays are sent to Austria-Hungary, 9,913 dollars and Belgium 23,633 dollars. North America, *i. e.* Canada, Mexico, Cuba, etc., use considerable quantities of fire and other clays, 117,181 dollars, South America purchases but little, 5,500 dollars.

Imports of Wares by United States. (Figure 5.) As an importer of wares of all kinds, the United States purchases the largest amount from Germany.

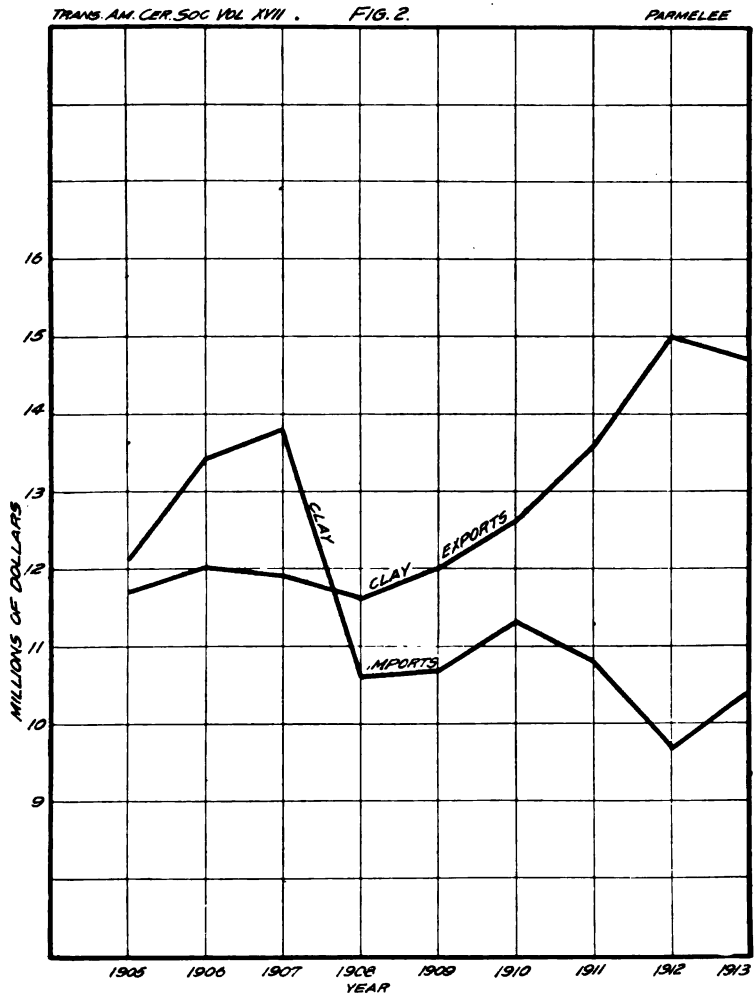
Fine wares	$3,743,518
Other wares	115,577
	$3,859 095=42 percent

Next in order stands the United Kingdom

Fine wares	$2,147,839
Other wares	291,573
	$2,439,412=27 percent

From France

Fine wares	$1,697,043
Other wares	7,398
	$1,704,441=18 percent


TRANS. AM. CER. SOC. VOL. XVII. FIG. 2. PARMELEE
MILLIONS OF DOLLARS
16
15
14
13
12
11
10
9
1905
1906
1907
1908
1909
1910
1911
1912
1913
YEAR
CLAY EXPORTS
CLAY IMPORTS

From Austria-Hungary

Fine wares	$ 651,771
Other wares	16,302
	$ 668,073 = 7 percent

From Belgium

Fine wares	$ 23,794
Other wares	37 857
	$ 61,651

According to statistics of 1912, (*Eng. Pottery Gazette,* 1914, p. 1074) we are Germany's best customer, taking about one-third of her export of wares. England takes only about one-seventh. Austria sends us about one-fifth of her exports, and to her next best customer (Great Britain) she sends about one-third.

Ninety-four percent of our importations consists of the finer wares, such as table ware, art ware, etc.

Exports by the United States. Table I. As shown previously, our export trade is steadily increasing. The larger part of the products is in the form of the coarser wares, brick, *etcetera,* which are taken by Canada and other neighboring countries in North America. Of the total exports

North America takes 90 percent
South America takes 5 percent

The classes of goods exported to North American countries are:

	percent
Fine wares	2
Coarse wares	8
Building brick	16
Fire brick	22
Teeth	2
Tiles (except drain)	16
Other wares	34
	100

TABLE I—EXPORTS OF WARES BY THE UNITED STATES IN 1913

TO	FINE WARES	COARSE WARES	BUILDING BRICK	FIRE BRICK	TEETH	OTHER WARES
	dollars	*dollars*	*dollars*	*dollars*	*dollars*	*dollars*
Austria-Hungary	83	3,076	....	....	....	....
Belgium	43	3,406	700	20	....	37,937
France	5,630	1,314	....	290	13,313	....
Germany	2,165	807	....	45	....	4,432
United Kingdom	15,872	....	....	2,368	5,019	6,619
North America	100,779	377,707	780,541	1,052,526	127,936	2,198,454
South America	4,387	43,962	3,586	32,591	2,266	180,475

TABLE III—EXPORTS BY THE UNITED STATES IN 1913 TO

WARE	ARGENTINE	BRAZIL	CHILI	COLOMBIA	PERU	VENEZUELA	BOLIVIA	ECUADOR	URUGUAY
	dollars	*dollars*	*dollars*	*dollars*	*dollars*	*dollars*	*dollars*	*dollars*	*dollars*
Teeth	918	461	....	700	....	....	....	....	....
Building brick	....	200	....	35	2,565	786	....	....	....
Fire brick	159	....	4,394	16,434	9,889	885	295	218	....
Chinaware	1,202	204	190	1,084	36	1,482	....	137	....
Earthen and stoneware	23,484	3,694	612	1,185	5,261	591	....	232	8,773
Tiles, except drain tile	135,068	6,723	1,225	372	284	6,085	....	180	6,006
Other wares		3,559	7,808	264	5,452	1,518	....	1,238	4,594
Totals	160,831	14,841	14,229	20,074	23,487	11,347	295	2,005	19,373

European countries to which we export goods stand in order of importance as follows:[1]

	percent
Belgium, miscellaneous wares, not classified	19.5
Great Britain, chiefly fine wares	18.0
France, chiefly teeth	9.5
Germany, fine and unclassified wares	3.2

Turning now to South America, the "Land of Promise" in the eyes of so many writers on the world's trade, we find our European competitors strongly entrenched. Unfortunately, we have been unable to secure recent statistics regarding the trade relations of France with these countries, and accordingly must confine our attention to imports from Great Britain, Germany, Austria-Hungary and the United States.

In this field, Great Britain is supreme. Her exports to the five principal countries — Argentine, Brazil, Chili, Peru and Uruguay—total nearly 3,000,000 dollars, while Germany's total is only about 1.000.000 dollars. The United States send about 200,000 dollars, Austria contributes only a very small amount. about 28,000 dollars. Table II.

TABLE II—EXPORTS OF WARES IN 1912

TO	UNITED KINGDOM	GERMANY	AUSTRIA-HUNGARY	UNITED STATES[1] 1913
	dollars	*dollars*	*dollars*	*dollars*
Argentine	1,330,230	357,500	14,500	160,831
Brazil	1,173,065	416,000	14,000	14,841
Chili	147,955	159,000	.....	14,229
Peru	116,870	.....	.....	23,487
Uruguay	130,295	.....	.....	19,373

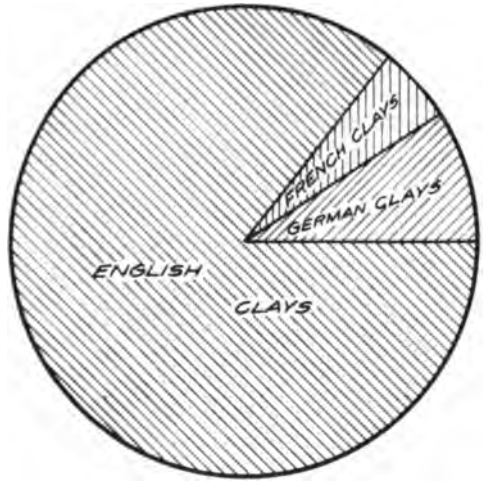
[1] NOTE—Statistics for the European countries for 1913 were not available when this was written.

The small share, which Germany[2] has secured in comparison with that of England, has surprised the writer, in view of the activities attributed to the German commercial agents on that continent. A study of the data covering a period of years, will throw light on that point.

[1] Exclusive of exports to North and South America.
[2] NOTE: It is not clear from the data at hand, that we have complete figures for Germany.

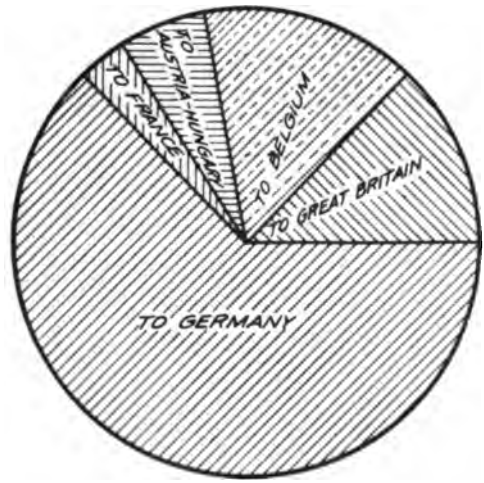
TRANS. AM. CER. SOC. VOL. XVII PARMELEE

FIG. 3.



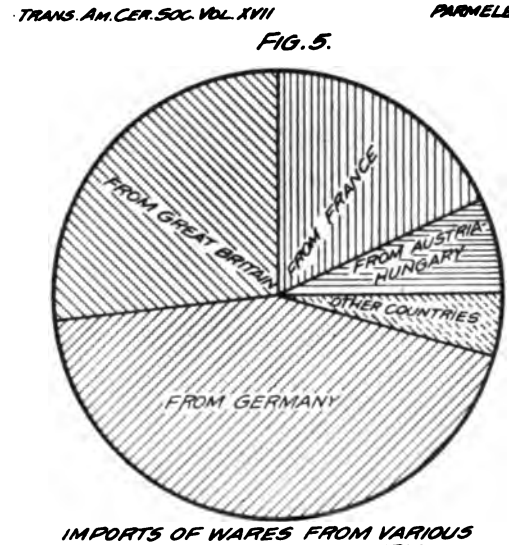
IMPORTS OF CLAYS BY THE UNITED STATES

FIG. 4.



EXPORTS OF CLAYS BY THE UNITED STATES

Of the five South American countries named, Argentine is the largest buyer, with Brazil a close second. These are followed in order by Chili, Uruguay and Peru. Semi-porcelains and similar grades of whiteware, constitute the largest item imported by each country. Sanitary ware is next, and stoneware third.



Insofar as our exports to South American countries during 1913 are concerned, we may group them as follows:

Argentine	$160,000
Peru	23 000
Colombia	20,000
Uruguay	19,000
Brazil	14,000

The largest purchaser of any single class of goods is Argentine, which took over 135,000 dollars worth of tile (not drain tile). The second largest purchase is earthen and stoneware, bought by the same country, to an amount approximating 23,500 dollars.

Colombia is an excellent customer for fire brick,—the third item of importance,—having a value of over 16,000 dollars.

In this brief analysis, I have endeavored to give you a glimpse of some of the trade conditions recently obtained in our relations with foreign countries. I do not feel competent, nor is it necessary, to consider ways and means for increasing our share of the world's trade. Men with long experience and expert knowledge of such matters have indicated the course which must be followed for the promotion of our national interests.

It is a matter of real interest, however, for the members of our organization to note these conditions. Unquestionably we are on the eve of great changes, which will be felt directly or indirectly by us all. New trade requirements, and large opportunities will bring new problems to the factory superintendent, and the ceramist. I have the confidence which I believe is shared by you all, that through the agencies of our schools of ceramics, and the long and useful service of the American Ceramic Society, that we have builded better than we knew to meet this opportunity.

ON THE FORMATION OF SOME BASIC SILICATES

BY E. D. CAMPBELL

When I was requested to talk to the Ceramic Society, my first idea was that I knew nothing about ceramics, and hence I would be rather out of place in speaking to this Society, until I realized that the scope of your work includes basic silicates, the hydraulic cements, so that it really covers the entire field of silica compounds. That gave me more or less excuse for coming before you. I do not think we realize that practically 50 percent of the accessible portions of the earth's crust is silica, hence the importance of silica in our environment, and that there can be no sharp line in the study of the compounds of silica. The passage of the study of the compounds of the acid silicates into the basic and so on, is a gradual one. Now perhaps instead of defining this talk as a theory of formation of some basic silicates, it might perhaps be as well to consider it as the evolution of an idea, resulting from research work we have been doing at the University, starting almost accidentally in the course of the work on Portland cement. We undertook some work, thinking it to be not quite as big a problem as it has developed into.

About 1899, at the time that the Portland cement industry began to assume importance in this State, we undertook some work, thinking it to be not quite as big a problem as it has developed into. We soon realized that in this comparatively new industry, as in all our modern industries, chemistry was at the foundation. It seemed to us that it would be a good thing if the University would start to contribute something to our knowledge of these underlying principles. It was with this idea in mind that we began research work, hoping to throw a little light on some of the conditions determining the constitution of Portland cement. The materials used at the beginning of the work were those that were actually used in commercial work, clays and shales, cement rock, etc. The object was to determine the relations existing between the chemical

composition and conditions of burning such as time, temperature, etc. We worked on this for three or four years, starting systematic experimental work involving, among other things, the development of a small experimental rotary kiln[1] only about three inches in diameter and about 34 inches long, but still one in which the conditions of time and temperature, and of course chemical composition, were under control. That was our first systematic work, following some preliminary work, and with this kiln we began to get a little information concerning conditions of formation of clinker. We were able to determine the temperation of formation of clinker, the temperature required for producing sound cement, and the relation between the acidity and the temperature required to produce sound and overburned cement; that is, those temperatures where there was danger of the clinker balling up or a ring forming on the lining of the rotary. Measurements made in 1902[2] have been verified to a gratifying degree by much larger scale experimental work carried on at the Bureau of Standards at Pittsburgh by P. H. Bates, and described by him in an article on "Some of the Properties of White Portland Cement," published in the Transactions of this Society last year.[3] With rotaries two feet in diameter and 20 feet long, a sort of a cross between an experimental and a commercial sized kiln, results were obtained by Bates, which confirmed very closely the temperature measurements of burning, which had been obtained in the chemical laboratory of the University of Michigan some ten years before. Following up, as we did, this work on temperatures of burning and some subsequent work on rates of hydration, etc., still the question came up to be solved, what is the constitution of the clinker? In his now classic work Le Chatelier, in the early 80's, showed that one of the principal constituents of clinker is a compound, to which he gave the name "tricalcic silicate." The existence of this, disputed so many years, is now settled beyond question as a constituent of cement.

In the earlier microscopic work which appeared mostly in

[1] *Jour. Amer. Chem. Soc.*, 1902, Vol. 24, 248.
[2] *Jour. Amer. Chem. Soc.*, 1902, Vol. 24, 969.
[3] *Trans. Amer. Cer. Soc.*, 1914, Vol. XVI, 551.

Europe in the last decade of the nineteenth century, attention was directed to what might be called the gross structure, that is, those aggregates of crystals constituting the main mass of the clinker as distinguished from the imbedding magma. It was shown that in normal clinker, the crystalline aggregate for which the term *alite* was suggested by Törnebohm, constitutes the principal part of the clinker, while most of the remainder is made up of an imbedding magma, for which Törnebohm suggested the term *celite*. Two other micro-constituents, which he termed *belite* and *felite*, were also described by him but are not usually present to any considerable extent in normal clinker. Although Le Chatelier maintained that the principal constituent of *alite* is tricalcic silicate, the fact that this compound had not been synthesized, led to doubt as to whether such a definite chemical entity existed or not. There is no longer any doubt that a definite compound with the empirical formula $3\,CaO.SiO_2$ does exist, but the question may be raised whether the three molecules of CaO bear the same relation to the silica or whether two may not be directly united to the silica forming a dicalcic silicate, the third molecule of calcium oxide being either lime of crystallization or possibly in solid solution. *Celite* has never been regarded as a single chemical entity but rather as a magma of undetermined constitution which promotes the separation or crystallization of the constituents which make up the *alite*.

The elaborate and painstaking researches which have been carried on for a number of years at the Geophysical Laboratory in Washington, seem to have had as their primary object the determination of the various chemical entities which would exist at different temperatures in systems of varying concentrations of silcia, lime and alumina. An enormous number of exact determinations have been made, showing the chemical entities which would co-exist when a given system had been brought to equilibrium by maintaining it for hours, days, or even weeks if necessary, at a given temperature, but as the material passing through a rotary cement kiln cannot have time to come to complete chemical equilibrium as a whole, may it not be possible that the progress of the chemical reactions taking place during

clinkering may be followed to advantage by studying systems of changing equilibrium?

In attempting to make a study of the chemical equilibrium that would take place in the cement clinker at a given temperature, we tried an experiment, thinking that if we would take pieces of clinker and hold these at a definite temperature for definite lengths of time we would be able to study the influence of time on crystal growth in the pieces of clinker so treated. With this experiment in mind some small pieces of clinker were

TRANS AM. CER SOC. VOL XVII FIG 1 CAMPBELL

TABLE OF MOLECULAR WEIGHTS OF CERAMIC MATERIALS AND OTHER SILICATES

	R_2O_3	SiO_2	RO	REFERENCES
PORCELAIN:				
SEVRES	100	280-350	30-35	BOURRY, CERAMIC INDUSTRIES, Pg 434
BERLIN	100	420-490	20-30	
FRENCH, BEST QUALITY	100	480-530	40-45	
CHINESE & JAPANESE	100	550-600	40-45	
" " "	100	620-740	30-40	
GLAZES:				
BERLIN	100	855	89	" Pg. 435
JAPANESE	100	804	180	
COKE BLAST FURNACE SLAG	100	300	600	
PORTLAND CEMENTS:				
IN GENERAL	100	300-600	800-2000	
CLINKER A	100	415	1380	J. IND AND E.C VOL 5, 1913, Pg 627
CELITE A_1 (1485°)	100	771	4876	
" A_3 (1510°)	100	993	4974	
" A_4 (1575°)	100	1082	4980	
ALITE A_1 (1475°)	100	1351 0	4008.0	
SYNTHETIC CELITE C_1	100	99.3	497.4	J. IND. AND E.C VOL 6, 1914 Pg. 706
CELITE ABS. FROM C_1	100	62.8	352.4	
CRYSTALS OF ALITE C_1	100	735.3	2365.0	
SYNTHETIC CELITE E_1	100	99.3	497.4	
CELITE ABS. FROM E_1	100	46.5	312.3	
CRYSTALS OF ALITE E_1	100	1786.7	5291.0	

placed in a crucible of pure magnesium oxide, which was then heated in a suitably designed furnace to a temperature slightly above that required to produce normal clinker, that is, above 1400°C., as previous work had shown to be necessary.

We had been working along this line for nearly a year when one of my assistants, Mr. E. G. Pierce, noticed that the crucible had become stained, and the pieces of clinker at the points of contact with the crucible had become porous and apparently dusted.

Although at first the significance of the stain was not appreciated, it soon became apparent that some constituent of the clinker must be in a very fluid condition at the clinkering temperature or it could not be drawn by capillary action into the pores of the magnesium oxide crucible which had not undergone any change in shape. The absorbed constituent, therefore, must have had low viscosity. That was the first suggestion of a means of separating constituents in a piece of cement clinker. Taking that as a starting point for systematic work, it became a matter of developing a suitable technique in order to utilize the principle suggested by the above experiment.

It was too late to do much that year, so the work of separating the fluid constituent from the non-fluid crystalline portion of clinker was taken up the next year. The full details of this work are given in an article on the "Constitution of Portland Cement Clinker."[4] The material we used and referred to later as clinker A in the table of Molecular Weights (Fig. 1). was made from a reground commercial mixture used in one of the Lehigh Valley mills. It was made into a clinker by taking the raw mixture and moulding it into disks about 30 mm. in diameter and about 20 mm. thick. This was burned at about 1525° to 1550° Centigrade so as to have a thoroughly well burned clinker. The parallel surfaces of the disks thus prepared were then ground smooth in order to give flat disks about 18-20 mm. in thickness and affording good contact with the absorbent disks which were made of pure magnesium oxide. These disks were made by mixing magnesium oxide, well shrunk by burning at about 1550°, with one-fourth its weight of unburned magnesium oxide and enough twenty-five percent solution of magnesium chloride to enable the mixture to be molded into disks. The disks thus prepared were again burned between 1530° and 1550°C., after which the parallel surfaces were ground smooth before using.

Small stacks consisting of a black center disk of clinker with two white magnesia disks above and two below were placed in a special gas fired furnace and heated to temperatures above

[4] *Jr. Ind. Eng. Chem.*, 1913, Vol. 5, 267.

that required for clinkering, for periods of from two and one-third to thirteen hours. The temperatures, which could be maintained constant within less than five degrees, were measured by means of a platinum rhodium thermo-couple, the bead of which was placed within three or four mm. of the clinker disk. In removing a stack from the furnace after an absorption, the magnesia disks were found to be nearly saturated with the fluid constituent, which had been absorbed by capillary action. The appearance of these stacks before and after the absorption is shown in Figure 2. Chemical analyses of the magnesia disks after the

FIG. 2

absorptions enabled the composition of the absorbed material to be determined. The portion of the clinker which becomes fluid at the clinkering temperatures, constitutes the *celite* as described by Tornebohm and Le Chatelier. Absorptions were made at a number of temperatures between 1475° and 1575°C. The molecular ratios of the acidic and basic oxides in the *celite* absorbed and in the *alite*, which constituted most of the unabsorbed clinker were calculated. From a study of the analyses and molecular ratios thus determined, the following facts seemed to be brought out: First: Although the proportion of ferric oxide,

(Fe_2O_3), to the alumina, (Al_2O_3), is a little higher in the *celite* than in the *alite,* the difference is not very marked, and the assumption that ferric oxide is molecularly equivalent to alumina, so far as the formation of *celite* goes, seems justifiable, although the hydraulic properties of the aluminates and ferrites differ. Second: With a given basicity of the mass as a whole, the proportion of silica to alumina and ferric oxide in the *celite* increases with the temperature. Third: With a given temperature, the proportion of the silica to the alumina and ferric oxide in the *celite* decreases as the basicity of the mass as a whole increases.

Because of these facts, the following hypothesis was suggested as to the changes taking place above 1400°C. during the clinkering process, and as to the constitution of the final clinker. First, that *celite* consists essentially of a calcium aluminate, fusible a little above 1400°C. and capable of dissolving when liquid, calcium ortho-silicate and calcium oxide. The calcium oxide is more readily soluble, and the solubilities of the ortho-silicate and the calcium oxide follow laws similar to those which govern the solubility of salts in liquid solution. Second, that *alite* consists essentially of either α or β calcium orthosilicate holding in solid solution calcium oxide with some calcium aluminate and ferrite. The concentration of the calcium oxide held in solid solution is dependent upon the basicity of the mass as a whole, and upon the temperature, but the limit of solubility apparently is reached when the proportions required to form the usually accepted tricalcic silicate have been reached.

If it were true that *celite* consists essentially of a fusible calcium aluminate or ferrate, in which both ortho calcium silicate and calcium oxide are soluble, their solubility, like that of most salts in aqueous solution, would be dependent upon the temperature, and it should be possible to synthesize a *celite* by properly proportioning the constituents, so that there should be a homogeneous solution nearly saturated at a temperature of. say 1575°C. From this solution crystals might be expected to separate, if the material was cooled slowly enough to a temperature below the saturation point, but still above the melting point

of the pure solvent. In order to test the validity of the above assumption, the next year's work was devoted to the synthesis of pure *celite,* that is, one containing almost no ferric oxide or magnesium since it was thought best not to complicate the problem at that time by having present constituents whose function in the clinkering of cement is still more or less a matter of discussion. The details of this work are given in an article on "Synthetic Celite and Large Crystals of Tricalcic Silicate."[5] Mixtures were prepared, having the ratio 100 R_2O_3 : 99.3 SiO_2 : 487.4 RO and melted in a large platinum crucible, platinum having been found to be the only material which would hold the

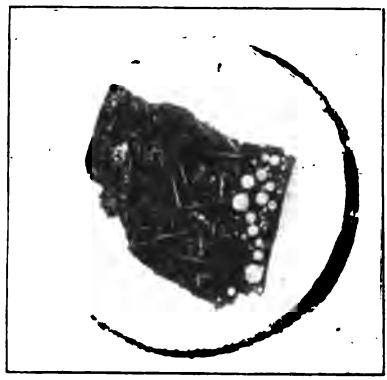


FIG. 3

very fluid melt and not react chemically with it. The molecular ratio selected for the synthetic *celite,* termed C-1, was that found by analysis for the fluid material drawn off at 1510°C. In order to insure complete solution, the temperature of the crucible was raised to 1575°C., at which temperature it was held from two to three hours and then gradually lowered to a little above 1400°, about six hours being required to bring it down to this latter point. The whole was then allowed to cool over night. A thin section of the slowly cooled material, showed it to consist apparently of long interlacing crystals imbedded in the magma from which they had separated during the slow cooling.

[5] *Jr. Ind. Eng. Chem.,* 1914, Vol. 6, 706

The structure of this section is shown in Fig. 3. In order to separate the imbedding magma or mother liquor from the crystals, weighed pieces were placed in a pure magnesium oxide dish which rested upon a number of pure magnesia absorbent disks similar to those used in the separation of *celite* from clinker. The temperature of the stack was raised to about 1470°, and after maintaining for three hours within five degrees

FIG. 4

of this point, the temperature was raised at the rate of 25 degrees per hour until it reached 1590°, when the whole was allowed to cool to room temperature. Thirty-three percent (33.44) of the weight of the material placed in the magnesia disk was recovered in the form of large thin plate-like crystals, some of them 7 mm. in length. which were proved by chemical analysis and optical properties to be tricalcic silicate, containing, either

FIG. 5

FIG. 6

FIG. 7

as a film on the surface or in solid solution, a small proportion of calcic aluminate with the formula of $5\ CaO : 3\ Al_2O_3$.

Side and top views of the stack after the absorption as well as of the mass of crystals and individual crystals are shown respectively in Figures 4, 5, 6 and 7.

Analysis of the magnesia disks showed the absorbed material to consist of a fusible aluminate together with calcium silicate and calcium oxide in such proportions that if the calcium silicate had all separated as tricalcic silicate, the aluminate would have had the formula $5\ CaO.3\ Al_2O_3$.

During the present college year, saturated solutions of calcium oxide in calcium aluminate were slowly cooled in an endeavor to determine whether well defined crystals of calcium oxide would separate out in a manner similar to the crystallization of tricalcic silicate. A mixture, having a molecular ratio of $4\ CaO.Al_2O_3$ was melted in a platinum crucible and cooled at the rate of 25° an hour from 1600° to 1400°C.

A section of the material showed that it had assumed the peculiar cellular structure first described by Quincke as characteristic of emulsions of immiscible liquids. In the case under examination, the cells contained calcium oxide, while the cell walls were made up of a fusible aluminate. A microphotograph of this section magnified one hundred diameters, as shown in Fig. 8.

In order to determine whether ferric oxide, Fe_2O_3, is capable of molecularly replacing Al_2O_3 in the formation of clinker, a synthetic *celite* termed "E-1," having the same molecular ratio, $100\ R_2O_3$, $99.3\ SiO_2$, $487.4\ CaO$, was prepared, the R_2O_3 consisting wholly of Fe_2O_3. After melting in a platinum crucible at a temperature of 1600°, it was slowly cooled to promote crystallization. A weighed portion of the dark brown mass was placed in a magnesium oxide dish, and an absorption made in a manner substantially similar to that previously employed for removing the mother liquor from the tricalcic silicate recovered in our former work. Thirty-one (31.4) percent of the weight of the mass was recovered in the form of thin, flat, plate-like crystals similar in form and, as subsequent examination showed,

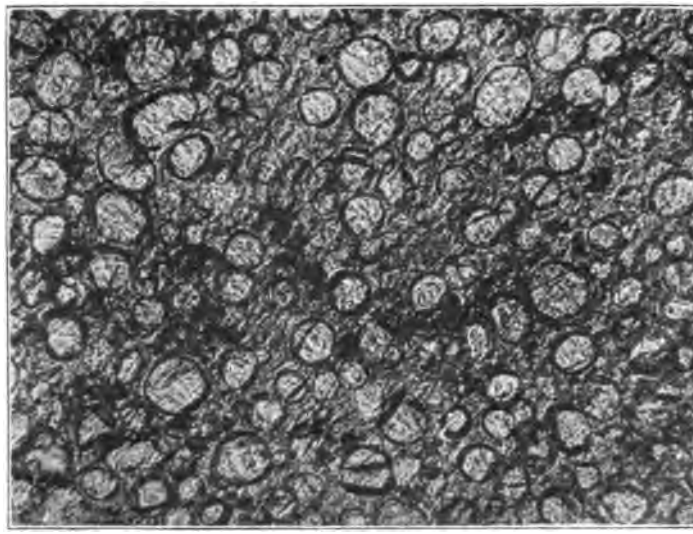


FIG. 8

FIG. 9

possessing the same optical properties as tricalcic silicate. These crystals were amber colored and analysis showed the total calcium oxide not quite sufficient to form tricalcic silicate, a small portion of the calcium oxide being apparently replaced by ferric oxide acting as a base. Top and side views of the stack before and after absorption are shown in Figures 9, 10 and 11, while the recovered crystals in mass and separated, are shown in Figures 12 and 13. This work, however, apparently demonstrated conclusively that in an oxidizing atmosphere calcium ferrate may function exactly like calcium aluminate so far as promoting recrystallization of calcium silicate goes, but the hydraulic properties of the ferrite are very different from those of the aluminate.

FIG. 10

FIG. 12

If, in the formation of basic silicates such as Portland cement clinker, we conceive the process as consisting of a series of solutions followed by recrystallization from a fusible solvent, until, if sufficient time is allowed, chemical equilibrium is reached. Might we not attempt to apply this same fundamental conception to account for the mechanism of reactions in ceramic materials? In attempting to apply this conception to ceramic materials, we must first consider the essential difference in chemical composition between the basic and acid silicates. The fundamental difference, as will be noticed from a study of the mole-

cular ratios in the table shown in Fig. 1, is due to the difference in relative mass of the RO oxides to SiO_2 and R_2O_3, resulting in a change of function of the R_2O_3. .In the basic silicates Al_2O_3 acts wholly as an acid oxide, and the fusible aluminate constitutes the solvent, by means of which recrystallization is affected; whereas in the acid silicates the Al_2O_3 acts as a basic oxide, and the solvent would almost necessarily be an acid silicate. The acid silicates are in general, much more viscous than the basic aluminates, but it seems to me, that bearing in mind the differ-

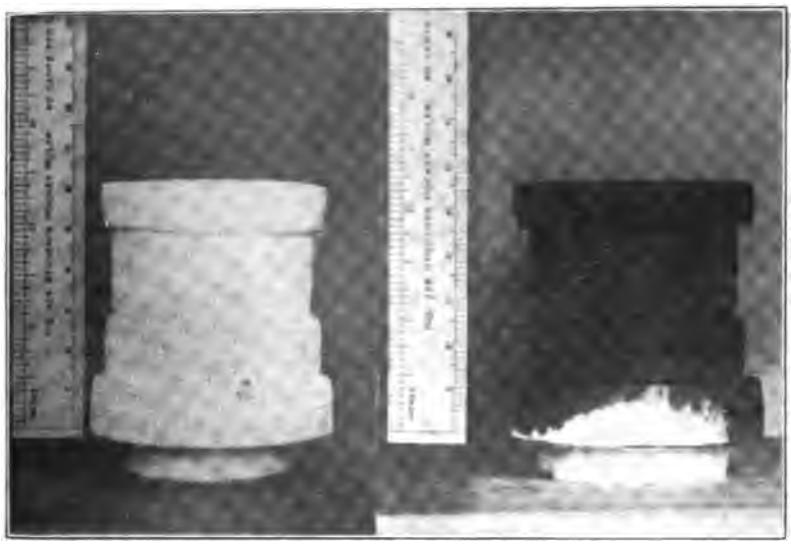


FIG. 11

ence in nature of the solvent, we might conceive the reaction going on in the burning of ceramic materials to consist similarly of a series of solutions and recrystallizations, which would progress until, in time, chemical equilibrium would be reached for any given temperature. Under this conception the study of the chemistry of ceramics would, like that of the basic silicates—and I might even add the constitution of metals—resolve itself primarily into a study of solubilities, as in ordinary solutions.

It is well known that the brilliant colors often shown on the feathers of birds, wings of insects and the spectrum from a Rowland grating are not due to the presence of a pigment but rather to the physical structure of the surface. In applying the hypothesis of solutions to glazes it is not difficult to conceive how substances might, on heating under certain conditions, pass into solution and recrystallize, the resulting crystals so orienting

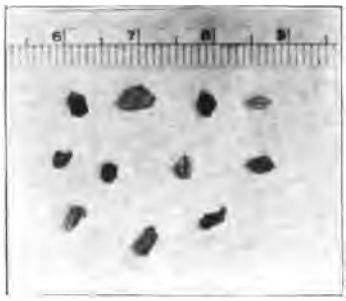


FIG. 13

themselves that the surface might possess a structure capable of affecting light and apparently possessing a color entirely independent of that which might be due to the chemical composition.

I would offer these ideas to your Society in the hope that they may prove of some service in furthering research in the scientific development of ceramics.

THE USE OF DEFLOCCULATING AGENTS IN THE WASHING OF CLAYS AND THE EFFECT OF THE PROCESS UPON THE COLOR[1]

BY G. H. BROWN AND W. L. HOWAT, PITTSBURGH, PA.

In the preparation of porcelain bodies in which American kaolins were used, it was found exceedingly difficult to produce a body of the desired whiteness and freedom from dark specks, due to the presence of small particles of impurities, and a body which would compare favorably as regards color with those of European manufacture. Although care was exercised in the preparation of the bodies to prevent the introduction of foreign particles during the blending, and although the body slip was passed through a 150 or 200 mesh sieve, still the particles were not removed to the desired extent.

The kaolins used were purchased from dealers in pottery materials and had been prepared at the mine by the usual washing and filter pressing processes.

By the employment of the usual methods of washing crude kaolins, most of the clay substance is held in suspension by the water and is carried into the settling tanks, but, in addition, small particles of impurities such as finely divided silica, biotite-mica. and other iron bearing minerals, when present, are also held up.

Deflocculation. Bleininger[2] emphasizes the importance of the use of caustic soda and other electrolytes in bringing about a condition of minimum viscosity which greatly assists in the separation of undesirable impurities from clay suspensions.

It is to be assumed that clays in suspension are in the dispersed state and consist of fine particles of clay substance which hold in suspension coarser grained materials. We know that by the addition of an alkali to a clay suspension or slip the degree of dispersion is greatly increased, with an accompanying increase in fluidity or decrease in viscosity. This increased dis-

[1] By permission of the Director, Bureau of Standards.
[2] *Trans. Amer. Cer. Soc.*, Vol. XV, page 343.

persion of the clay particles caused by the addition of the alkaline electrolyte decreases the quantity of coarse grained material which the clay is able to hold in suspension, and, as a result, much of this foreign material is precipitated. This point may be illustrated by placing a quantity of clay in the slip state in each of two graduated tubes. To one slip a determined amount of caustic soda is added, and both tubes after thorough shaking are allowed to stand. It will be noted that in most cases the clay will remain in suspension for a longer time in the tube to which the electrolyte has been added, and that a greater quantity of coarser particles will settle to the bottom of the tube than from the clay to which no electrolyte has been added. The latter clay will also show signs of settling before the former.

It has been found, that a definite quantity of alkali added to a clay suspension is required to bring about the maximum degree of dispersion of the clay particles, and that the addition of an acid or salt caused decreased dispersion, or brought about flocculation. Addition of a too small or an excessive amount of alkali does not produce a sharp separation. The allowable variation in the amount of alkali to be added is great enough, however, to permit its addition on a commercial scale.

The removal of a foreign material from a clay suspension depends somewhat upon the physical character of the material. Thus Bleininger found, that it was not practical to remove finely disseminated ferric hydroxide from a clay suspension to which an electrolyte had been added. The same would apply to other colloidal materials.

As an illustration of the practical application of the removal of fine grained material from a clay, a sample of slip from a kaolin which had been washed by passing through the usual series of settling troughs was placed in each of two 500 cc. graduated tubes. To one tube 0.06 percent of caustic soda was added, and both tubes were thoroughly shaken and allowed to stand. Within a few seconds fine grained material was being precipitated to the bottom of the tube to which the alkali had been added, and this continued vigorously until a precipitate of 1 cm. depth was formed. After standing for one hour there was no

precipitation in the tube, to which no alkali was added. The material which settled out from the washed clay was composed chiefly of fine grained silica, and passed a 150 mesh sieve without residue.

Georgia Kaolin. Porcelain bodies in which the clay substance was partly introduced as a certain brand of Georgia kaolin were found to contain particles of impurities which were very objectionable. It was also known that the same clay had been giving trouble in one pottery due to the introduction of black specks. Some shipments of the kaolin were more objectionable for this reason than others, the washing process employed at the mines being somewhat erratic.

A twenty-five pound sample of the Georgia kaolin was taken from stock and blunged in a large ball mill for several hours. Portions of the slip were placed in 500 cc. bottles, and caustic soda in amounts varying from 0.05 percent to 0.25 percent were added to the respective bottles. The bottles were thoroughly shaken and allowed to stand for one-half hour. In this way, it was determined that an addition of 0.17 percent of caustic soda produced dispersion such that the clay slip attained maximum fluidity and produced the rapid settling-out of the coarser particles accompanying such a condition.

The slip was placed in a large stoneware jar, 0.17 percent by weight of caustic soda was added, and the slip thoroughly stirred. After allowing to settle for one-half hour, the material in suspension was siphoned off, passed through a 150 mesh sieve, and aluminium chloride added, the flocculated material being filter pressed. Discs 10 cm. in diameter were made by pressing the rewashed kaolin in plaster molds. For purposes of comparison, discs were also prepared from the kaolin as received from the clay dealers. Bodies having a composition of 50 percent clay, 30 percent flint and 20 percent spar were made up from the kaolin and the unwashed material and were molded into 10 cm. discs.

The test pieces molded from the kaolin and from the bodies were fired, unglazed, to cone 10 in closed saggers. The test pieces molded from the rewashed kaolin and the body containing the rewashed kaolin were markedly superior in color and freedom

from specks to those molded from the kaolin taken from stock and not rewashed.

North Carolina Kaolin. The deflocculation tests on Georgia kaolin were duplicated on a sample of North Carolina kaolin taken from stock, in the same manner, the quantity of caustic soda necessary to produce the desired dispersion being about 0.19 percent. Test pieces were molded as before and fired to cone 10. The North Carolina kaolins appear to respond more quickly to the action of the alkali, the coarser material settling out rapidly.

Although the stock North Carolina kaolin produced a whiter color than the Georgia and contained fewer particles of dark burning impurities, a noticeable improvement in color and cleanness was evident in the test pieces molded from the rewashed material.

Florida Kaolin. Florida kaolin appears to respond less readily to the action of the alkali than either the Georgia or North Carolina kaolins. The deflocculation tests were conducted as before on a sample purchased on the market. The amount of alkali added was 0.14 percent, although some difficulty was experienced in determining just what quantity to add. The Florida kaolin usually produces a very good, white color, although it sometimes may contain some dark colored impurities which produce objectionable dark specks in the finished piece.

The test pieces produced from the rewashed kaolin and fired to cone 10 were slightly improved in color and were markedly free from the black specks brought out in the test pieces molded from the clay as received from the dealer and used without rewashing..

Tennessee Ball Clay No. 3. In addition to the characteristic dark or buff color produced in the burning of ball clays, dark colored specks due to the presence of particles of impurities are in evidence. On account of the great plasticity and the consequent difficulty of washing, ball clays are placed on the market in the crude state. In addition, the washing of ball clays is discouraged, owing to the supposed decrease in plasticity accompanying the washing process.

The washing tests on the Tennessee No. 3 ball clay were

conducted in a somewhat different manner than for the kaolins. The ball clay was ground, screened and blunged in a ball mill for a short time. To the mill charge 0.4 percent by weight of hydrochloric acid was added, and the blunging continued for several hours. The slip was placed in a stoneware jar and allowed to settle. The supernatant liquid was then siphoned off and discarded, and the clay again blunged with a supply of fresh water to which was added 0.15 percent by weight of caustic soda. After standing for one hour, the suspended matter was siphoned off, flocculated by an addition of aluminium chloride and filter-pressed.

A number of 10 cm. discs were molded from bodies composed of 50 percent ball clay, 30 percent flint and 20 percent spar, the washed ball clay being used for one body and the crude ball clay for another. The discs were fired to cone 9 in closed saggers.

The body prepared from the washed ball clay, although showing the characteristic buff color of this type of clay, was much improved as regards clearness of color and freedom from specks due to iron bearing minerals. The buff color is also slightly lightened in the bodies prepared from the rewashed clay.

Means of measuring the increase or decrease in plasticity of the washed ball clay were not at hand, although so far as could be observed from the working qualities of the two materials there was but small difference in plasticity.

General Effect of Deflocculation Upon Color. Obviously, in most cases, the degree to which the color and general appearance of a clay is improved by the employment of deflocculating agents is a factor of the original purity of the clay and the excellence of the washing treatment to which it is submitted at the washing plant. Clays occur, however, which, although of poor color, cannot be improved by the employment of deflocculating agents on account of their physical constitution.

Washing tests on samples of English kaolins to which deflocculants were added did not produce noticeable improvement in color, owing to the original purity of the materials or the ex-

cellence of the washing treatment. Of the three varieties of American kaolins subjected to the deflocculating treatment, as stated before, the Georgia kaolin showed the greatest improvement as regards color. The improvement in the North Carolina and Florida kaolins was not so noticeable, although the gain was well worth the expense of the treatment.

Effect of Deflocculation upon Drying and Burning Shrinkages. The drying and burning-shrinkages of kaolins and bodies are affected somewhat by the use of the deflocculating agents. The average shrinkage measurements in the Table I were made upon 10 cm. discs which were prepared from the kaolins and bodies by pressing in plaster molds. The discs were dried at 110°C. and fired in saggers to cone 10.

TABLE I—SHRINKAGES IN PERCENT OF DRY LENGTH—CONE 10

	DRYING SHRINKAGE	BURNING SHRINKAGE
A—100 PERCENT CLAY		
	percent	*percent*
Florida kaolin (as received)	7.55	12.45
Florida kaolin (washed)	7.30	12.70
North Carolina kaolin (as received)	4.75	5.4
North Carolina kaolin (washed)	3.70	6.92
Georgia kaolin (as received)	4.60	12.75
Georgia kaolin (washed)	3.90	15.20
B—50 PERCENT CLAY, 30 PERCENT FLINT, 20 PERCENT SPAR		
Florida kaolin (as received)	5.45	7.9
Florida kaolin (washed)	4.75	9.15
North Carolina kaolin (as received)	3.05	7.4
North Carolina kaolin (washed)	2.20	8.75
Georgia kaolin (as received)	4.05	9.45
Georgia kaolin (washed)	2.60	9.10

It will be noted that the addition of the alkali caused a decreases in the drying-shrinkages of the test pieces containing the kaolins which were subjected to the washing treatment. The decrease in drying-shrinkage is most noticeable in the body containing the washed Georgia kaolin.

Treating the kaolins with the electrolyte, however, increases the burning-shrinkage of the test pieces, with the exception of the body containing the treated Georgia kaolin. This increase in burning-shrinkage is probably due to the removal of the fine grained non-plastic materials from the kaolins and to the presence of a proportionately greater amount of clay substance.

Loss of Material Due to Rewashing. The additional percentage of material removed from kaolins by the employment of deflocculants is determined with some difficulty from an intermittent treatment and is apt to give misleading results. Undoubtedly the employment of an electrolyte produces a cleaner and sharper separation of the clay substance from the non-plastic materials. The clay substance adhering to the grains of quartz, *etcetera,* is set free and is not carried down with the precipitated material to such a great extent as in the ordinary washing process. The additional percentage of non-clay substances removed by the deflocculating process is undoubtedly balanced in part by an increased yield of clay substance.

Applications. When the use of an electrolyte is desirable, it may be added to the crude kaolin at the clay washing plant or to the washed kaolin at the factory by the use of additional blungers. The addition at the clay washeries is to be preferred on acount of the smaller expense, and likelihood of a better separation and a greater uniformity of the product.

At the present writing the electrolyte treatment is used commercially at a washing plant producing clay for the paper industry. The electrolyte is added to the blunger at relatively small expense, and a clay is produced which is greatly improved in color and freedom from grittiness over that produced by the former washing treatment without the addition of an electrolyte.

Conclusions. By the employment of the deflocculating treatment with caustic soda or silicate of soda, kaolins may be improved as to color, the improvement being more marked in some than in others. Some clays respond readily to the alkali treatment, while others are more sluggish. Impurities present as objectionable specks may be removed by this treatment.

The increased quantity of non-clay substance removed is

partly balanced by an increased production of clay substance due to the sharper separation.

Rewashing of the kaolins is accompanied by changes in the drying and burning-shrinkages of the kaolins and bodies into which they are introduced. In this investigation, a decrease in drying-shrinkage and an increase in burning-shrinkage was noted.

The increase or decrease in plasticity accompanying the electrolytic process was not determined.

The deflocculation treatment is being used in producing a product of improved quality in a clay-washing plant producing clay for the paper industry.

DISCUSSION

Mr. Purdy: How much more expensive is this treatment going to make our kaolin?

Mr. Brown: We had some figures on that; I think that in one plant where they were adding 0.06 percent of the alkali about six cents a ton would be added to the cost.

Mr. Purdy: That is for materials only?

Mr. Brown: For the materials.

Mr. Purdy: How about the increased cost of handling?

Mr. Brown: It did not involve any increase in labor or equipment in the plant I have in mind.

Mr. Mayer: What do you do with the clay you cannot use?

Mr. Brown: In a washing plant equipped with blungers and troughs, according to our experience, we do not lose so very much clay on account of the sharper separation and the increased amount of clay which goes into suspension, although there is more non-plastic material thrown out. I made the statement in my paper, that in tests made in the laboratory, we could not determine accurately the percentage of clay discarded on account of the small batches we were handling at the time. We could not siphon off all the material in suspension.

Mr. Binns: Wouldn't there be at least one percent rejected?

Mr. Brown: Yes.

Mr. Binns: More than that?

Mr. Brown: Well, I think that would depend upon the material.

Mr. Watts: At what stage of this washing process is the addition made?

Mr. Brown: The electrolyte is added at the blunger.

Mr. Watts: The plan then is to wash the clay by the customary method through the floating tanks, and the electrolyte is added in the final blunger prior to being filter pressed.

Mr. Brown: Preferably the electrolyte is added at the beginning of the washing process before going into the blunger.

Mr. Watts: Then you would add the electrolyte at the outlet of the mica settling troughs; would that be the idea?

Mr. Brown: Well, it would be some place in that neighborhood; of course all washing plants are not alike. In the washing plant I had in mind, they had only one blunger followed by long troughs. The clay was dumped into a large blunger and from there passed into the troughs and finally into the settling tanks, but the alkali was added in the blunger.

Mr. Watts: It would then be added at that stage of the process where the crude mass of kaolin entered the washing process?

Mr. Brown: In this case it was, although I should think that you could vary the system somewhat to fit the conditions at the plant; that is, it might be added a little further along.

Mr. Watts: My reason for asking the question was this: we know that even in the best regulated kaolin washing plants there is a certain amount of undesirable material which comes down with the kaolin, and at the same time there is a certain amount of kaolin lost because of the fact that it sticks to the particles of mica and sand which settle. By introducing the alkali in the washer or whatever they use as a substitute for blunging up the kaolin, prior to this treatment through the mica-settling troughs and the sand settling troughs, would you get the 100 percent of actual kaolin which the crude material contains and would the settling out of the undesirable materials be improved?

Mr. Brown: I think it would. In one plant where we tried

this process, after adding the electrolyte some difficulty was experienced in removing the sand. The sand packed very tightly in the troughs, in fact it was necessary to put in extra baffles to catch the sand, and we ascribed that to the freedom of the sands from clay substance, and for this reason and from tests in the laboratory, we think the separation is much sharper and that really more of the clay substance is separated and less settled out with the non-plastic materials.

Mr. Watts: Was any note made as to whether the total production of kaolin by this process was materially changed. With the two processes did they produce actually about the same amount of kaolin?

Mr. Brown: Yes; we have their statement that practically the same amount was produced.

Mr. Binns: I understand that there is enough clay substance disentangled from the coarse material to compensate for the coarse material rejected?

Mr. Brown: Yes, that's the idea.

Mr. Binns: Has any observation been made as to the effect of the process on plasticity?

Mr. Brown: No, we have not made any measurements as to the change in plasticity.

Mr. Purdy: May I ask if more kaolin is not lost through the filter press by this method than before?

Mr. Brown: Not necessarily. It is customary to flocculate the clay after subjecting it to the electrolytic treatment.

Mr. Purdy: You deflocculate and the reflocculate before pressing?

Mr. Brown: Yes; that is the practice now in many of the plants; they flocculate their clay even where they do not use the electrolyte.

Mr. Purdy: So by this method, you would have to have another treatment.

Mr. Brown: Yes. Am I not right in that, Mr. Watts?

Mr. Watts: Yes.

Mr. Purdy: May I ask if this water is all wasted?

Mr. Brown: No; the water may be used again.

LABORATORY METHODS FOR THE PHYSICAL TESTING OF FIRE CLAYS.

BY C. H. KERR, R. J. MONTGOMERY AND C. E. FULTON

In the physical testing of fire clays there has been to date but little agreement in opinion as to the kinds of tests required and the correct ways of making such tests. In every issue of the transactions of this Society various tests are recorded which aim to disclose the particular properties the author wished to emphasize, but there has been little or no attention paid to a study of the requirements of testing from the standpoint of bringing out the general characteristics of a fire clay.

In all technologic work in the testing of fire clays, the proposed use must be borne in mind. A test which for one particular user is of exceedingly great importance, especially in connection with any peculiarities in his methods of handling the material, may be of little or no consequence to another manufacturer. But in general, the examination of fire clays, for whatever purpose, must be carried out along more or less standard lines. After this general classification has been made, special tests may be applied to determine the value of a clay for a particular purpose. In most cases these final tests must be made in the plant under factory conditions, and it is only after a very thorough acquaintance with the types of clays used that factory operation may be controlled from the laboratory.

Many of the tests enumerated below give important information regarding the behavior of the material that is essential in judging the clay for any possible use commercially and also give a means of checking up the uniformity of shipments of clays received. If complete information is required in regard to the material, the full line of tests must be completed.

The following is a list of the usual tests made on a fire clay:

1. Tests of the raw clay.
   - (a) Description.
   - (b) Sieve test.
   - (c) Specific gravity.

(d) Plasticity.
(e) Drying shrinkage.
(f) Modulus of rupture.

2. Tests of the burnt clay.
(g) Burning shrinkage at various temperatures.
(h) Modulus of rupture at various temperatures.
(i) Apparent porosity at various temperatures.
(j) Apparent specific gravity at various temperatures.
(k) True specific gravity at various temperatures.
(l) Open and closed pores at various temperatures.
(m) Fusion point.

Tests of Raw Clays. (a) Description. The first thing in the examination of any fire clay is to note its general nature, especially texture, color and feel, and also any peculiarities of a geologic nature, such as fracture and structure.

(b) Sieve Test. We have found the sieve test to be very satisfactory for ordinary testing purposes, and the more elaborate and difficult elutriation process is usually unnecessary in practical testing work.

The "wet sieve test" is used, and the details are as follows: 75 to 100 grams of clay are washed through a 200 mesh sieve. The sieve with residue is placed in a warm place until the residue is dry. The regular sieve test is then made on this residue using the Tyler Standard screen scale testing sieves,[1] the openings being based on the Rittinger ratio (factor 1.414). A careful examination of the various residues often gives much information as to the origin and nature of the clay.

(c) Specific gravity. The specific gravity determination is seldom made on raw clays, and in our estimation it is of little value, for usually the variation in specific gravity in clays of the same type is very small. Furthermore the variations in specific gravity of the raw clay have not been found to be directly related

[1] Cf. *Trans Amer. Cer. Soc.*, Vol. XV, 375-80 (1913).

to variations in burning behavior of clays of the same type. When such determinations are made, the method used is the same as that discussed under true specific gravity of burnt clay given later in this paper.

(d) Plasticity. Many methods of measuring plasticity have been advanced, and some of these are of considerable importance in special investigation work. It is our opinion that clays of the same type when made up with water to their best working consistency may be judged by the sense of the feel and classified as having poor, fair, good or excellent plasticity, and it is our opinion that if in addition the other properties of the raw clay are considered at the same time, the manufacturer may intelligently determine whether a certain clay has a plasticity satisfactory for his use.

The amount of water required to form a plastic mass should be determined, but this figure should not be taken as an exact index of plasticity. It has been found, that for a uniform clay the water required to obtain the best working consistency may be checked very closely by different observers, if these observers are familiar with clay handling. The determination should be made on an air dried sample and results expressed as:

$$\frac{Cc.\ Water}{Gr.\ of\ clay\ used} \times 100 = Percent\ water\ for\ plasticity.$$

Distilled water should be used, as small amounts of salts in solution have a marked effect on the results. To make the work complete a determination of the mechanical moisture in the air dried sample should be made by drying at 110°C, but this should not be added to the water required to make the air dried sample into a plastic mass. These two figures must be considered independently.

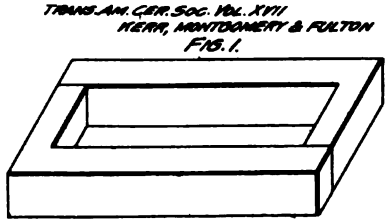
In this and all subsequent work, the raw clay is ground to pass a 20 mesh sieve (wire .0172 in., hole .0328 in.).

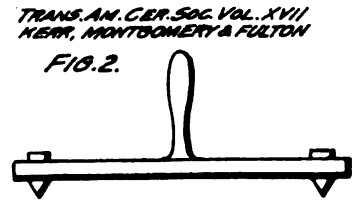
(e) Drying Shrinkage. Ordinarily the linear shrinkage only is measured. The plastic mass is molded into bars 1¼ by ¾ by 5 inches. The molds used are made of brass, are in two parts shaped as shown in Figure 1, and the parts are held together by an ordinary iron screw clamp with a four inch

opening between the jaws.

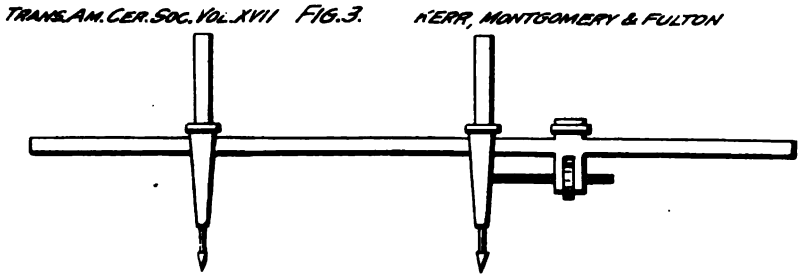
The bars can be made very rapidly with a little practice. The mold is wiped with an oiled cloth from time to time to prevent sticking.

Shrinkage marks are stamped on the bar 100 millimeters apart, the holes being made by sharp conical steel points as shown in Figure 2.





The bars are allowed to dry seven days in the laboratory and are then placed in an oven, first at 75°C. and finally at 110°C.; six to eight hours are required at each temperature.[1] The drying shrinkage is then measured (after the bars are cooled), by a form of trammel beam carrying conical points sharper than those used in making the original marks. Figure 3 shows this measuring device.



This trammel has a screw adjustment (A) which insures perfect centering and consequent accuracy in measurement. The actual shrinkage is then measured off the trammel on a steel scale graduated in 0.5 of a millimeter, and the percent shrinkage is read directly from the scale, being estimated to 0.1 percent.

[1] Cf. *Trans. Amer. Cer. Soc.*, XV, 358, 1913.

Volume shrinkage is often a valuable determination for special investigations, but for ordinary technologic testing it is too difficult of manipulation, and in such work the results are not of greater practical value than the ordinary linear shrinkage. To obtain good results with this determination, the work should be done in a room in which a nearly constant temperature can be maintained, as small temperature changes will cause serious errors in any determination where the volume of a liquid is measured.

(f) Modulus of Rupture. Bars of the same size as mentioned above are air dried for seven days, then dried to constant weight at 75°C. and further to constant weight at 110°C. These are cooled and broken in a standard make of modulus of rupture machine. The one used in this laboratory is of the shot type, and loads from 8 to 700 pounds can be applied. This allows the same machine to be used for both raw and burned bars. Very fine grained clays of high plasticity are apt to give a low strength in the modulus of rupture test, although from their appearance and density, greater strength might be expected. This is probably due to the development of minute cracks during drying.

Owing to the variation in the shrinkage of fire clays, each test piece, after being broken, should be measured both in thickness and in width with micrometer calipers to 0.001 of an inch. The extreme fiber stress or modulus of rupture is then figured from the regular formula:

$$\textit{Modulus of rupture} = \frac{3\,P\,l}{2\,b\,d^2}$$

where P=The load applied in pounds.

b=The width of the test piece in inches.

d=The thickness of the test piece in inches.

l=The distance between supports in inches.

With a five inch bar, four inches between supports is very satisfactory. With l equal to four inches the formula changes to,

$$\textit{Modulus of rupture} = \frac{6\,P}{b\,d^2}$$

The modulus of rupture test gives a very good idea of the

strength of a body in the green state, and is of especial value where high percents of grog are used.

Tests of the Burnt Clay. The following tests are made on the fire clay burned to a series of cone temperatures which cover the most important range. For each special purpose, a proper selection of cones should be made, but for general fire clay testing (especially the plastic fire clays) the data should include determinations for temperatures ranging from cones 01 to 20 and usually cones 01-4-8-12-16-20 will be found to be very satisfactory. The burning is done in small circular flame furnaces. A description of these is given by Mr. C. E. Fulton in Volume XVI, page 386, of these Transactions. Bars of same size as mentioned before are thoroughly dried and piled in the furnace in an open checker work three layers deep with eight bars to a layer. The cone pat of three consecutive cones (one below and one above the cone temperature desired) is placd on the lower layer about half way between the center and the outside of the pile. Three burns are made at each temperature, extending over a period of about eight hours. The bars of the clay tested are placed in a different layer in each burn, thus eliminating variations that might be due to position in the furnace. Oxidizing conditions are maintained in all burning work. When the bars are to be burned above cone 1, they are first given a very slow calcining burn to cone 010, thus requiring an extra day for the burning. This is to prevent cracking of fine grained clays in burning and permits faster heating up when burning to higher temperatures, thus giving better control during the latter part of the burn.

While it is generally understood that a short fire in a laboratory furnace will not compare with a long fire in a commercial kiln, clays can be readily compared on a short fire basis and the general characteristics of the clay will be brought out. Of course very little can be predicted as to color.

(g) Burning Shrinkage. The linear shrinkage is measured at each cone temperature, and by subtracting the drying shrinkage for each particular bar, that caused by burning is obtained. The method used is the same as that used in connection with drying shrinkage.

(h) Modulus of Rupture. After the shrinkage is measured, the bars are broken in the transverse machine. They are measured for width and thickness, and the modulus of rupture is figured as given in connection with the testing of the raw clay.

The strength usually increases until vitrification is well progressed, and the porosity is practically zero. The bar then becomes brittle and loses in strength. Loss in strength at the higher temperatures may also be due to overfire or to cracks developed during the cooling of the well vitrified piece.

(i) Apparent Porosity. After breaking in the modulus of rupture machine, small parts of the bars (about 15 grams) are broken off, weighed dry, boiled for one hour in water, cooled, and the wet and suspended weights are obtained. The apparent porosity is calculated from the formula:

$$\textit{Percent porosity} = \frac{W-D}{W-S} \times 100$$

Where D=The dry weight of the test piece.

W=The wet weight of the test piece.

S=The suspended weight of the test piece.

Boiling for one hour is found to give higher and more consistent results than soaking for any period and seems to be as satisfactory as the use of a vacuum. The simplicity of the determination is in its favor, and the results may be checked within a few tenths of one percent on the same piece with repeated determinations.

(j) Apparent Specific Gravity. The apparent specific gravity may be figured from the weighings obtained in determining the apparent porosity by the following formula:

$$\textit{Apparent specific gravity} = \frac{D}{D-S}$$

(k) True Specific Gravity. In order to calculate the open and closed pore space developed in burning, the true specific gravity of the burned bars must be known. We have found the ordinary cement bottle method of determining specific gravity to be applicable to burnt clays. The pycnometer method may be more accurate under very accurate laboratory control and in the

hands of a very skilled operator, but in the average laboratory, the pycnometer specific gravity results are valueless. With the cement bottle, the determination may be made much more quickly, and results can be checked within one unit in the second decimal place. This is well within the limits of the other sources of error. Three determinations are made at each cone temperature, and the average is taken.

The method is as follows: The parts of the bars remaining from the three burns are ground together and fine enough to pass a sixty-five mesh sieve. The ground sample is dried at 110°C. and placed in a glass stoppered bottle until used. The specific gravity bottle is filled with gasoline to the lower mark and placed in a water bath, a gallon crock being very satisfactory. The entire system, as well as the sample to be tested, should be at room temperature, which should change very little during the determination. Gasoline is used as it allows the burnt clay to settle readily to the bottom of the flask. The gasoline should be introduced through a funnel to prevent wetting the sides. The level of the gasoline should be noted, and the bottle allowed to stand in the bath until it comes to a constant point. About 50 grams of the sample is now weighed out (the weight being determined to the third decimal place), a final reading of the gasoline level in the bottle is taken, and the sample is slowly introduced. A piece of glazed paper should be used to hold the sample. The bottle is left in the water bath during filling, and in case of clogging, the bottle is gently tapped until the material settles to the bottom. When the entire sample is in the bottle is removed from the water bath and tapped with the fingers until air bubbles cease to come to the surface. It is then returned to the bath, the stopper placed in the bottle and allowed to stand until a constant reading is secured on the upper scale.

The true specific gravity is obtained by the formula:

$$\frac{\textit{Weight of the sample}}{\textit{Volume of the sample}} = \textit{True specific gravity}$$

The size of grain of the sample used will effect the results. especially when the clay overfires and the volume of the closed pores is large. Table I gives the effect of 65 mesh (hole .0082 in..

wire .0072 in.) and 150 mesh (hole .0041 in., wire .0026 in.) grinding for a St Louis fire clay.

TABLE I

Cone	01	4	8	12	16	20
65-mesh	2.723	2.720	2.697	2.679	2.659	2.617
150-mesh	2.720	2.718	2.714	2.706	2.688	2.663

While this difference seems rather large, the open and closed pore spaces when calculated give an actual variation that is very small. Table II gives the open and closed pores based on the specific gravity determinations in Table I.

TABLE II

Cones	01	4	8	12	16	20
	65 Mesh					
	percent	*percent*	*percent*	*percent*	*percent*	*percent*
Closed pores	6.4	7.4	9.5	11.2	12.2	13.3
Open pores	12.8	7.4	3.4	2.1	4.3	10.4
True clay volume	80.8	85.2	87.1	86.7	83.5	76.3
	100.0	100.0	100.0	100.0	100.0	100.0
	150 Mesh					
Closed pores	6.0	7.2	9.8	11.7	13.1	14.7
Open pores	12.8	7.4	3.4	2.2	4.4	10.4
True clay volume	81.2	85.4	86.8	86.1	82.5	74.9
	100.0	100.0	100.0	100.0	100.0	100.0

The maximum variation is 1.4 percent and the average is about 0.5 percent. In most cases the increased accuracy of the 150 mesh grinding is of little value, and the 65 mesh material is much more easily prepared and handled.

Open and closed pores. The final calculations are made as follows:

(1) $$\frac{D}{\text{True specific gravity}} = \text{True clay volume.}$$

(2) $$(D-S) - \frac{D}{\text{True specific gravity}} = \text{Volume of closed pores.}$$

(3) *W—D=Volume of the open pores.*

When *D*=The dry weight of the sample,

S=The suspended weight of the sample,

W=The wet weight of the sample.

If 1, 2 and 3 are added together and calculated to percentages the relative proportions of the three are obtained.

(m) Fusion Point. Small cones of standard shape are made up, and the fusing point is determined against Seger cones as usual. In determining the temperature, however, we find that the time interval is of importance in connection with the ordinary visual comparison of the cones. Readings are taken of the time when the cone starts to bend and the time when the tip touches the pat. These are compared with similar readings taken for standard cones. In this way, very accurate fusing point determinations may be made.

DISCUSSION

Prof. Parmelee: You burn your samples in the small furnace in a very short time?

Mr. R. J. Montgomery: Yes, sir.

Prof. Parmelee: How do the results compare with the results of burning the same materials during a longer period to the same temperatures?

Mr. R. J. Montgomery: The average length of a burn for temperatures below cone 1 is about eight hours. For burning above that temperature, we first give all test bars an eight hour calcining burn to cone 010 and then a second eight hour burn to the desired cone temperature. While burning in a laboratory furnace will not check commercial burning, we find that two clays burned in the laboratory can be compared directly.

Prof. Parmelee: What is the purpose of that calcining burn?

Mr. R. J. Montgomery: The main object is to prevent the cracking of fine grained clays in the final burn. In the calcining burn the heat is applied very slowly. In the final burn the temperature is raised quite rapidly at first and slowed down as the final temperature is reached in order to obtain an even distribution of heat.

Mr. Smith: If you want to test for brick would this test of yours give the shrinkage so that a man could make his die for a dry pressing machine?

Mr. R. J. Montgomery: In making this test the amount of water used would give what we would call maximum plasticity. If you require a stiffer mix, you would have to take the percent water into consideration when using the shrinkage determination. It is only after a very thorough acquaintance with the types of clays used that laboratory results can be applied directly to factory operation.

Mr. Stover: I would like to make one suggestion. When you make a series of tests for the practical potter or brick maker, you use laboratory kilns and laboratory methods, and the data obtained cannot be directly applied to the industries. I believe scientific data of this character should be so presented that the practical man could understand and handle it.

Mr. Longnecker: I would like to ask if the boiling test would be equal to a vacuum test?

Mr. R. J. Montgomery: We have never directly compared the boiling and vacuum test for apparent porosity. Boiling one hour will give a higher value than soaking forty-eight hours and will give results that may be checked repeatedly on the same sample.

TESTS OF IOWA FIRE CLAYS

BY M. F. BEECHER

The purpose of this investigation by the Iowa Engineering Experiment Station was to determine the possibility of utilizing Iowa clays for refractories. Some attempts have been made in the state to manufacture fire-brick, and at the time of starting this work there was at least one clay manufacturing plant that was contemplating entering the fire-brick line. Iowa has never been recognized as a fire clay producer, and it was to determine to what extend the qualities of Iowa clays would warrant the development of fire-brick plants, that these tests were undertaken.

While the general term fire-clay includes clays of great variety, it was not the intention of the present investigation to cover the whole field, but rather to limit the work to such clays as showed some possibility of possessing refractory quality. A large number of No. 2 or easily vitrifying fire clays (of which Iowa has quite a number) were therefore included. The most refractory clays of the state were obtained and the results of the tests on such are given in this paper.

In all, twenty-three clays were sampled for tests; nineteen belonging to the Coal Measures, two to the Cretaceous, one to the Maquoketa and one which seemed to be a somewhat impure kaolin, judging from its appearance and from the results of the tests. These clays were selected largely on the strength of their local reputations and from the results of preliminary tests. It may reasonably be assumed that this list contains all of the most refractory clays of the state.

The tests consisted in determining the shrinkage, drying behavior, total and apparent porosity, bulk, apparent and true specific gravity, warpage, fusion point and action under load at high temperatures.

Fusion Point. The fusion points were determined by means of cones made up from a carefully prepared sample of each clay. The fusions were made in a carbon resistance furnace,

essentially the same as that described by Bleininger and Brown in Volume XII, *Trans. Amer. Cer. Soc.* The temperatures were determined by means of an electric pyrometer, except in the case of three clays where cones were used. In most cases, four or more cones of each clay were tested, and the value given in Table I is the average of the values obtained.

TABLE I—FUSION POINTS OF IOWA CLAYS

CLAY NO.	FUSION POINT		LOCALITY
	DEGREES CENTIGRADE	CONES	
20	1247	6	Mystic, Appanoose County.
21	1249	6	Clermont, Fayette County.
22	1486	18	White City, Monroe County.
23	1445	16	White City, Monroe County.
24	1220	4½	Mystic, Appanoose County.
25	....	30	Deep Creek Township, Clinton Co.
26	1572	22	Danville, Henry County.
27	1550	21	Redfield, Dallas County.
28	1516	19+	Colfax, Jasper County.
29	1475	17	Colfax, Jasper County.
30	1535	20	Ft. Dodge, Webster County.
31	1554	21	Lehigh, Webster County.
32	1522	19½	Lehigh, Webster County.
33	1556	21+	Lehigh, Webster County.
34	1590	23	Fairfield, Jefferson County.
35	1537	20½	Morgan Valley, Marion County.
36	1600[1]	24+	Denova, Henry County.
40	1550	21	Eldora, Hardin County.
41	1600	23½	Eldora, Hardin County.
42	1575	22	Eldora, Hardin County.
43	....	21½	Sargent's Bluff, Woodbury County.
44	....	27	Sargent's Bluff, Woodbury County.
77	1430	15	Adelphi, Polk County.

[1] Cone started.

Warpage. The determination of the warpage was made according to the method pursued by Worcester and Orton[1] in the study of roofing tile clays. The clays were made into bars ½ in. by 1 in. by 9 in. by hammering out on a bat and cutting into

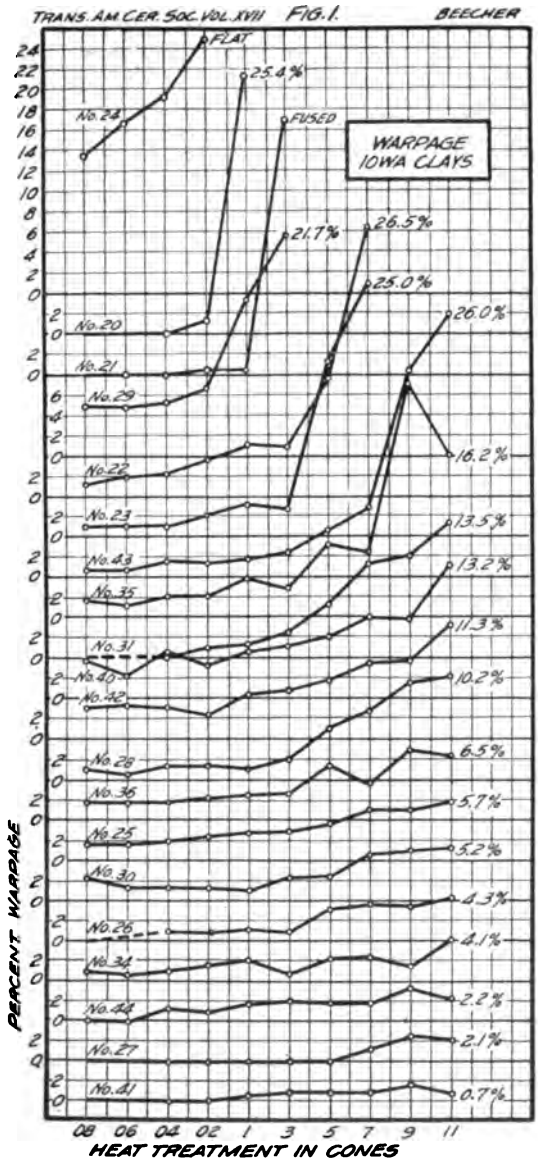
[1] Fourth Series, *Bul. 11, Ohio Geological Survey.*

strips. After drying, any initial warpage was noted, and the bars were supported on fire clay knife edges placed seven inches apart in saggers made for the purpose. The saggers were then fired to cones 08, 06, 04, 02, 1, 3, 5, 7, 9 and 11. The percent warpage was calculated, as the amount of sag divided by the distance between the knife edges. The results are tabulated in Table II, and a graphical presentation offered in Fig. 1.

On the basis of the fusion and warpage results, ten clays were selected for further tests. These were Numbers 25, 26, 27, 31, 34, 35, 36, 41, 43, and 44.

TABLE II—WARPAGE

CONE	08	06	04	02	1	3	5	7	9	11
CLAY										
20	....	....	....	1.4	25.4	....	....	....	....	....
21	....	....	....	0.5	0.4	fused	....	....	....	....
22	1.3	2.0	2.3	3.7	5.1	5.0	11.8	26.5	....	....
23	1.0	1.1	1.2	2.2	3.2	2.8	17.3	25.0	....	....
24	13.5	16.7	19.3	flat	....	....	....	....	....	....
25	1.6	1.6	2.0	2.3	2.8	2.8	3.6	5.0	5.0	5.7
26	....	....	0.9	0.9	1.1	0.9	3.2	3.5	3.5	4.3
27	....	....	....	....	....	....	....	1.2	2.4	2.1
28	1.0	0.6	1.5	1.5	1.2	2.1	5.0	6.8	9.6	10.2
29	5.0	4.8	5.3	6.7	15.4	21.7	....	....	....	....
30	2.3	1.3	1.3	1.2	0.9	2.3	2.4	4.6	4.9	5.2
31	....	....	0.3	1.0	1.3	2.5	5.4	9.3	10.1	13.5
32	....	....	....	....	....	....	....	....	....	....
33	....	....	....	....	....	....	....	....	....	....
34	0.8	0.6	1.0	1.6	2.1	0.7	2.1	2.5	1.5	4.1
35	1.7	1.2	2.1	2.1	3.9	3.0	7.2	6.6	23.2	16.2
36	1.8	1.8	1.8	2.3	2.5	2.7	5.5	3.7	6.9	6.5
40	3.7	2.3	4.5	3.3	4.5	5.1	6.1	8.0	7.8	13.2
41	....	....	....	....	0.4	0.9	0.8	0.9	1.6	0.7
42	3.0	3.3	3.1	2.3	4.3	4.7	5.7	7.5	7.7	11.3
43	0.7	0.7	1.4	1.4	1.8	2.5	4.7	7.0	20.4	26.0
44	....	....	1.1	0.9	1.7	2.0	1.8	1.7	3.2	2.2


TRANS. AM. CER. SOC. VOL. XVIII FIG. 1. BEECHER
WARPAGE IOWA CLAYS
FLAT
FUSED
No. 24
No. 20
No. 21
No. 29
No. 22
No. 23
No. 43
No. 35
No. 31
No. 40
No. 42
No. 28
No. 36
No. 25
No. 30
No. 26
No. 34
No. 44
No. 27
No. 41
25.4%
21.7%
26.5%
25.0%
26.0%
16.2%
13.5%
13.2%
11.3%
10.2%
6.5%
5.7%
5.2%
4.3%
4.1%
2.2%
2.1%
0.7%
PERCENT. WARPAGE
08 06 04 02 1 3 5 7 9 11
HEAT TREATMENT IN CONES

Shrinkage. For the determination of shrinkage, porosity and of specific gravity, a number of bars measuring 1 in. by 1 in. by 4 in. were made up from each clay. These were fired at cones 1, 3, 5, 8 and 10, except in three cases where circumstances necessitated making the burns approximately five cones lower. The results of the shrinkage measurements are given in Table III.

TABLE III—SHRINKAGE

CLAY NO.	25	26	27	31	34	35	36	41	43	44
					Drying					
	5.5	3.5	5.2	1.9	3.5	1.9	7.5	4.4	2.7	4.1
Cone										
04	9.0	...	...	...	5.5	...	10.0	...	...	...
02	10.0	...	...	...	6.2	...	11.5	...	...	...
1	11.0	...	8.0	2.0	6.2	5.0	12.5	5.7	5.0	6.0
3	12.0	5.0	8.0	2.5	6.2	5.5	11.0	5.7	5.2	6.0
5	13.5	6.0	8.0	3.0	6.2	6.5	12.5	6.0	6.2	6.5
8	....	6.9	8.0	3.5	...	7.0	....	6.5	6.1	6.5
10	....	6.2	8.5	3.5	...	6.0	....	6.2	5.3	6.2

Porosity. Two porosity values were determined—apparent and total. The apparent porosity was obtained from weight of trial piece after immersing in water which was kept boiling for 45 minutes.

$$100 \times \frac{saturated\ weight - dry\ weight}{saturated\ weight - suspended\ weight} = apparent\ porosity.$$

The total porosity was calculated from the specific gravities, thus:

$$\text{Percent total porosity} = 100 \times \left(1 - \frac{bulk\ sp.\ gr.}{true\ sp.\ gr.}\right)$$

The porosity data is given in Tables IV and V.

Specific Gravity. The bulk specific gravity was obtained by the usual method of suspension, whence

$$\text{Bulk sp. gr.} = \frac{dry.\ wgt.}{sat.\ wgt. - susp.\ wgt.\ of\ sat.\ specimen}$$

FIG. 2a

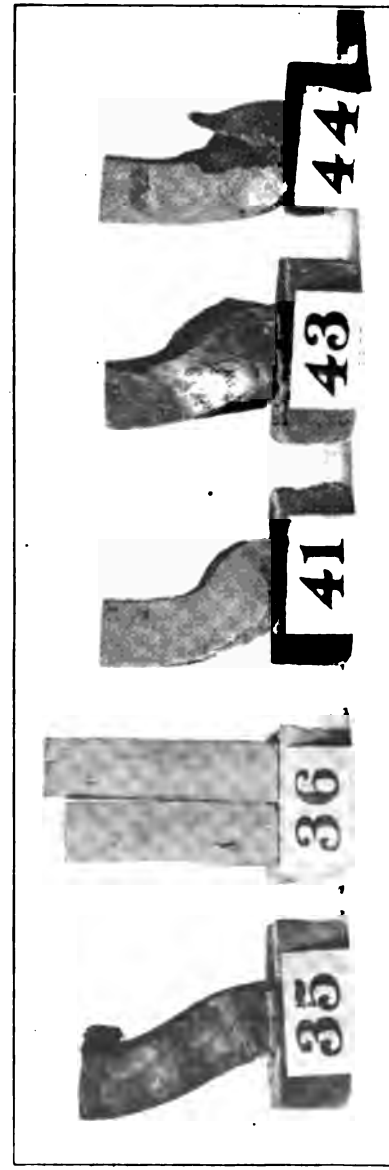


FIG. 2b

From the dry and suspended weight was obtained the apparent specific gravity, thus:

$$\text{Apparent specific gravity} = \frac{\textit{dry. wgt.}}{\textit{dry wgt.} - \textit{susp. wgt. of sat. specimen}}$$

The true specific gravities were determined by means of a pycnometer with the usual calculation—

$$\textit{sp. gr.} = \frac{W}{V} = \frac{W}{W - (W'' - W')}$$

where W=the weight of the sample used, W' the weight of the bottle filled with distilled water, and W'' the weight of the bottle, sample and water. Owing to the inconsistency of the results obtained by the usual method, the following methods was used. (The ordinary possibilities of error were greatly increased, since the bottles used were of a cheap grade, not true in shape and with unground mouths.)

TABLE IV—APPARENT POROSITY—PERCENT

CLAY NO.	25	26	27	31	34	35	36	41	43	44
Cone										
1	31.4	....	16.1	30.0	24.8	17.3	19.0	22.9	18.6	21.2
3	26.3	17.1	12.9	30.1	22.3	13.6	15.4	20.3	14.7	17.0
5	21.4	11.5	10.9	26.5	21.1	11.2	10.0	23.1	13.3	11.2
8	....	7.7	9.8	22.6	....	4.7	....	17.8	5.2	9.4
10	....	7.9	10.0	21.6	....	17.2	....	17.5	6.6	11.4

TABLE V—TOTAL POROSITY—PERCENT

CLAY NO.	25	26	27	31	34	35	36	41	43	44
Cone										
1	36.3	....	19.7	31.0	28.0	24.0	25.1	25.1	21.1	23.5
3	28.3	22.5	18.3	30.1	24.9	20.8	22.1	24.5	21.6	21.9
5	24.6	19.5	19.0	27.9	21.0	17.6	17.3	24.0	17.3	21.1
8	....	15.5	16.1	24.8	....	14.0	....	18.1	11.8	13.7
10	....	16.0	16.0	23.5	....	22.6	....	18.7	19.8	13.4

Each bottle was first filled with distilled water, and its weight, suspended in distilled water determined on a chemical balance. A five to seven gram sample was weighed out in the dry bottle to avoid loss in transfer. The bottle was then half filled with distilled water, placed over a flame and boiled for ten minutes. The neck and sides were then washed down and the bottle nearly filled with boiled distilled water. When it had cooled to room temperature, the filling was completed, the stopper fitted, and the weight of the bottle as it was suspended in distilled water, again obtained. By the formula given above, the true specific gravity was calculated, W'' and W' both being suspended weights. The consistency with which the results of duplicates agreed with the originals, indicated that this method did away with practically all the difficulties encountered in the usual method. In nearly every case two samples agreed within .006.

This method requires fewer delicate operations, and the careful wiping of the bottle after filling becomes unnecessary. Accuracy is independent of any change in the volume of the bottle. It has the one disadvantage, that there is less accuracy in weighings taken to the fourth decimal place in grams, of bodies in suspension, since the beam is rendered less sensitive by the suspending medium.

The specific gravity data is tabulated in Tables VI, VII and VIII.

Load Test. The load test was made in a manner substantially as outlined by Bleininger and Brown[2], with the exception that the total time of test was six hours. Table IX shows the results as obtained. Figure 2 illustrates the manner in which the failures occurred. A glance at the results given in Table IX will make evident the severe limitations upon the manufacture of refractory material from Iowa clays.

[2] *Tech. Paper No. 7, Bureau of Standards.*

TABLE VI—BULK SPECIFIC GRAVITY

CLAY NO.	25	26	27	31	34	35	36	41	43	44
Cone										
1	1.82	....	2.16	1.85	1.92	2.03	2.01	2.00	2.13	2.04
3	1.96	2.05	2.16	1.86	1.98	2.09	2.09	2.00	2.14	2.07
5	2.09	2.12	2.15	1.90	1.98	2.17	2.19	2.00	2.24	2.07
8	....	2.19	2.19	1.94	....	2.15	....	2.04	2.25	2.13
10	....	2.17	2.20	1.97	....	1.92	....	2.04	2.13	2.14

TABLE VII—APPARENT SPECIFIC GRAVITY

CLAY NO.	25	26	27	31	34	35	36	41	43	44
Cone										
1	2.65	....	2.58	2.64	2.57	2.45	2.48	2.60	2.62	2.68
3	2.47	2.47	2.48	2.66	2.54	2.42	2.46	2.50	2.50	2.49
5	2.66	2.40	2.41	2.59	2.51	2.45	2.44	2.60	2.58	2.34
8	....	2.37	2.42	2.51	....	2.24	....	2.48	2.46	2.35
10	....	2.46	2.47	2.51	....	2.32	....	2.48	2.28	2.41

TABLE VIII—TRUE SPECIFIC GRAVITY

CLAY NO.	25	26	27	31	34	35	36	41	43	44
Cone										
1	2.750	.....	2.688	2.679	2.667	2.673	2.682	2.671	2.702	2.666
3	2.737	2.645	2.643	2.664	2.635	2.640	2.683	2.650	2.731	2.651
5	2.770	2.635	2.654	2.634	2.609	2.635	2.649	2.631	2.709	2.625
8	.....	2.592	2.612	2.581	.....	2.599	.....	2.587	2.652	2.568
10	.....	2.585	2.621	2.575	.....	2.581	.....	2.607	2.655	2.572

TABLE IX—RESULTS OF LOAD TEST ON IOWA FIRE CLAYS

CLAY NO.	EMPIRICAL FORMULAE				CONE OF FUSION	SHORTENING UNDER LOAD	DEFORMATION STARTED DEG. C.	TIME OF TEST	LOCATION ON LUDWIG'S CHART	CONES DIFF.
	SILICA	ALUMINA	R O	TITANIUM						
								minutes		
25	1.99	1.00	.096	.050	30	$\frac{7}{32}$	1190	360	35	—5
26	7.03	....	.193	.115	22	buckled	1065	300	29	—5
27	5.60	....	.285	.066	21	crushed	1090	315	29	—5½
31	4.36	....	.235	.062	21	crushed	1050	229	30	—6½
34	8.88	....	.316	.090	23	$\frac{18}{32}$	1150	360	..	.....
35	6.14	....	.447	.084	20½	buckled	1010	205	28	—5
36	4.69	....	176	.075	24+	$\frac{21}{32}$	1180	360	31	—6
41	8.48	....	.301	.091	23½	crushed	1050	300	..	.....
43	7.03	....	.921	.080	21½	crushed	1025	262	..	.....
44	7.93	....	.308	.113	27	crushed	1065	300	..	.....

DISCUSSION OF RESULTS

The apparent porosity values as plotted upon Purdy's chart (Fig. 3) show no regularity of agreement. Of the four clays largely within the No. 1 curves, only one (Clay No. 25) should be so classed on the basis of fusion point, action under load and warpage. No. 31 and No. 41 are clearly not of the quality indicated by the chart.

Some reason for this disagreement is suggested from a study of the total and apparent porosity values. From an inspection of that data, it is found that several clays would locate more in agreement with the chart, relatively to one another, on the basis of total porosity. For instance, No. 36 is too low and No. 41 too high, but the former has much the larger amount of sealed pores. However, even such a reconstruction would not correct such discrepancies as Nos. 31 and 36 present.

In like manner the apparent specific gravities plotted upon the specific gravity chart, (Fig. 4) present even less satisfactory results. This, however, is suggested by Purdy[3] himself, since the specific gravities vary by smaller numerical amounts and consequently allow for less accurate differentiation. But the same disturbing factor of sealed pores enters into the determination of the apparent specific gravity as in the apparent porosity and affects the results in a similar manner.

Empirical Formulae. In Fig. 5 is presented Ludwig's diagram with such of the Iowa clays plotted as would come within the limits of the figure. The fusion points thus indicated, vary from the actual fusion points by from five to six and a half cones. This variation seems at first a little surprising, especially since some investigators have obtained rather close agreement.[4] But assembling the analyses of 60 fire clays with known fusion points and plotting their empirical formulae upon the diagram it was found that only six accurately agreed, 22 more agreed by 1 cone or less and the remaining 32 varied by from 1½ to 6 cones. There were 10 cases of variation by more than 4 cones.

[3] *Bul. 9, Illinois State Geological Survey*, page 273.
[4] Purdy and Moore, Vol. IX, *Trans. Amer. Cer. Soc.*, p. 312.

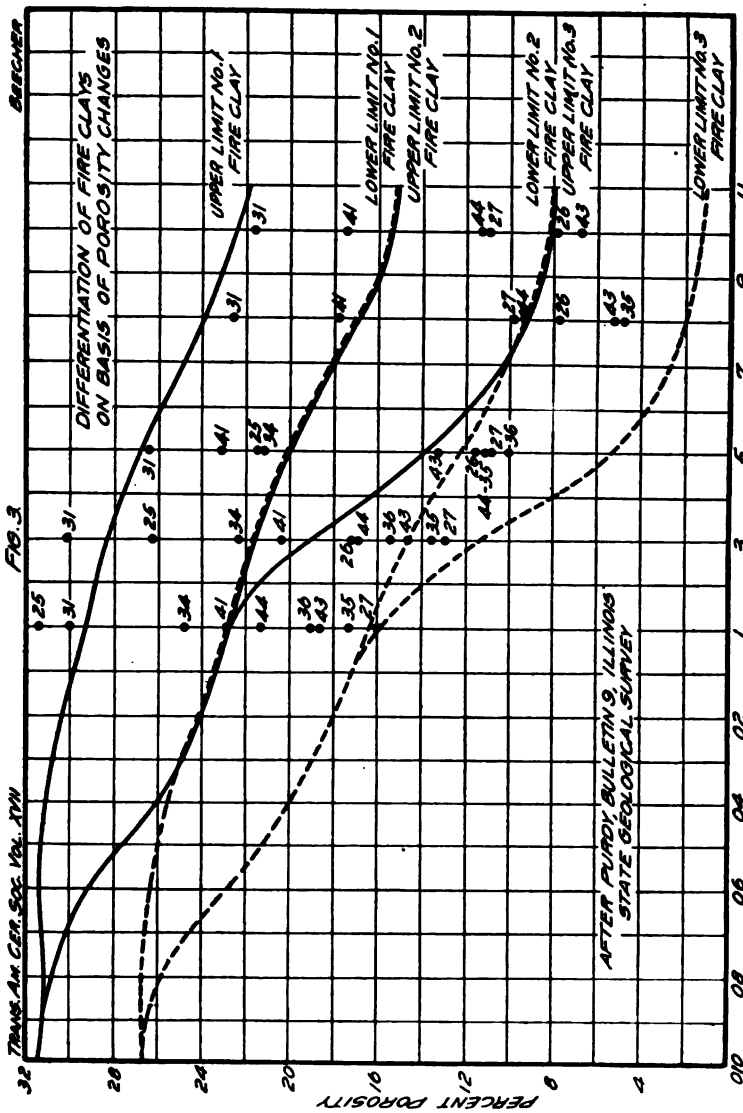


FIG. 3
TRANS. AM. CER. SOC. VOL. XVII
BEECHER
DIFFERENTIATION OF FIRE CLAYS ON BASIS OF POROSITY CHANGES
UPPER LIMIT No. 1 FIRE CLAY
LOWER LIMIT No. 1 FIRE CLAY
UPPER LIMIT No. 2 FIRE CLAY
LOWER LIMIT No. 2 FIRE CLAY
UPPER LIMIT No. 3 FIRE CLAY
LOWER LIMIT No. 3 FIRE CLAY
AFTER PURDY, BULLETIN 9, ILLINOIS STATE GEOLOGICAL SURVEY
PERCENT POROSITY
HEAT TREATMENT - CONES

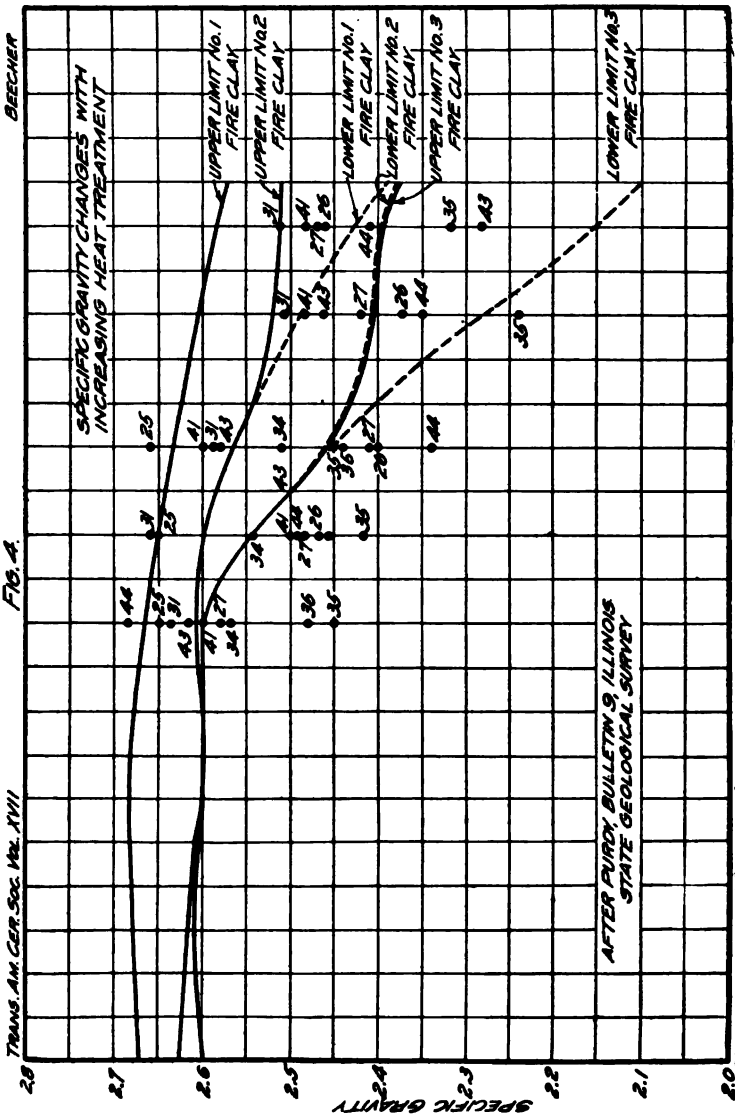
An inspection of Table X indicates that, in general, the fusion point is lowered as the silica and R O increase, but that this rule cannot be applied with any exactness to clays in particular, and points out the likelihood of error in attempting to judge fusion point on the basis of the empirical formula.

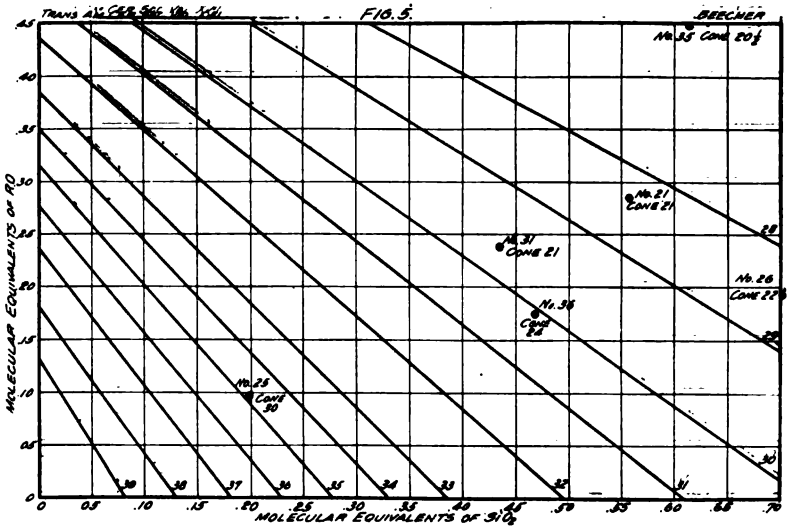
This difficulty in the differentiation of fire clays on the basis of specific gravity changes and empirical formulae lies in our meager knowledge of the exact mineralogical constitution of clays and of the compounds or eutectics formed during vitrification. A study of the volume changes of most minerals on melting or fusion, will indicate the great dependence of both the direction and amount of the specific gravity change, upon the identity of the constituent minerals present. For example, quartz on inverting to tridymite at 870° increases in volume 16.9 percent; tridymite on inverting to cristobalite at 1470° decreases 2.1 percent; and cristobalite on fusing at 1600° increases 4.75 percent.[5] Sillimanite on inverting to cyanite above the melting point decreases 15.5 percent. The albite-anorthite series on fusing increases 2.4 percent at the anorthite end and 9.4 percent at the albite end. The cases cited are some of the extremes that may be found, but they make it at once evident that specific gravity changes are not of the greatest value unless the identity of the minerals present is known.

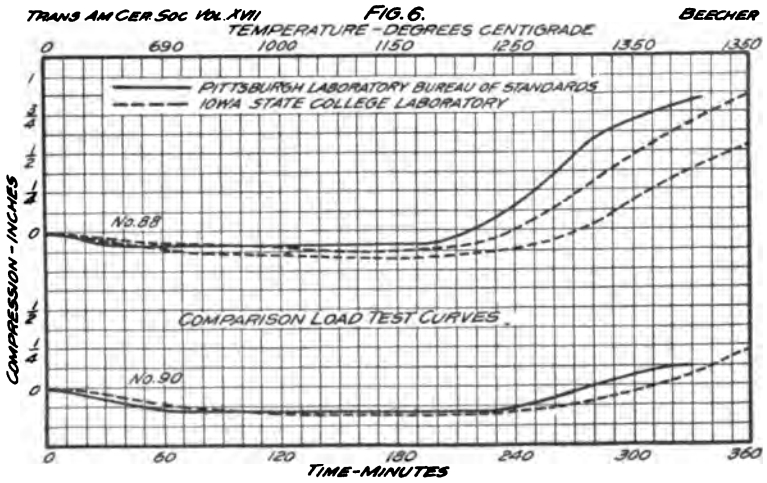
Load Test Data. In order to correlate the present work with that already published by the Bureau of Standards, it is possible, through the courtesy of Professor Bleininger, to present in Fig. 6 a comparison of curves taken in the two laboratories. The tests were made on two different brands of commercial fire brick. The specimens tested in both laboratories were selected from the same stock, and as far as could be judged from appearance were about the same as regards structural density, degree of burning, etc.

Some marked dissimilarities may be noted. (The later compression indicated by the dotted curves is due only to the longer time of test.) The solid curve shows a "quiescent period"[6] dur-

[5] Fenner, *Am. Journal of Science*, 4th Series, Vol. 36, page 331.
[6] Bleininger and Brown, *Trans. Amer. Cer. Soc.*, Vol. XII, page 355.


BEECHER
SPECIFIC GRAVITY CHANGES WITH INCREASING HEAT TREATMENT
UPPER LIMIT No.1 FIRE CLAY
UPPER LIMIT No.2 FIRE CLAY
LOWER LIMIT No.1 FIRE CLAY
LOWER LIMIT No.2 FIRE CLAY
UPPER LIMIT No.3 FIRE CLAY
LOWER LIMIT No.3 FIRE CLAY
SPECIFIC GRAVITY
HEAT TREATMENT. - CONES
AFTER PURDY, BULLETIN 9, ILLINOIS STATE GEOLOGICAL SURVEY
TRANS. AM. CER. SOC. VOL. XVII
FIG. 4.


TRANS AM CER SOC VOL XVII
FIG. 5.
BEECHER
No. 35 Cone 20
No. 21 Cone 21
No. 31 Cone 21
No. 26 Cone 22
No. 36 Cone 22
No. 25 Cone 30
MOLECULAR EQUIVALENTS OF RO
MOLECULAR EQUIVALENTS OF SiO2


TRANS AM CER SOC VOL XVII
FIG. 6.
BEECHER
TEMPERATURE - DEGREES CENTIGRADE
PITTSBURGH LABORATORY BUREAU OF STANDARDS
IOWA STATE COLLEGE LABORATORY
No. 88
COMPARISON LOAD TEST CURVES
No. 90
COMPRESSION - INCHES
TIME - MINUTES

ing a large part of the second, third and fourth hours which is not evident in the dotted curve, nor was it evident in any of the sixty odd tests made in the Experiment Station laboratory. The flattening of the curve at the finish of the test was found to obtain in all the tests made at the Station, though in Fig. 6 this flattening does not appear as pronounced as in the curves of the Bureau of Standards. This decrease in the rate of deformation of the brick would naturally be expected because of the increased cross-section and the greater density of the brick (evidenced by a smaller volume after the test, as calculated from scale measurements).

The degree to which it is possible to duplicate a given load test under the same conditions is indicated by the two dotted curves for specimen No. 88. It seems altogether probable that individual bricks may vary to the extent indicated by the curves.

Clay No. 31 is of particular note. It maintains a high porosity and high specific gravity throughout the heat range, it fused at cone 21 and crushed under load at 229 minutes when the test had reached 1230°. The brick from the load test showed no signs of vitrification or flowage and was soft and friable. This clay is either a freak, or it suggests the possibility of a fourth group of fire clays that are non-refractory and non-vitrifying, non-vitrifying in the sense that they do not vitrify at temperatures that are reached in commercial kilns and not implying that vitrification does not take place before fusion is reached. The simple classification suggested is as to refractory and non-refractory with a vitrfying and non-vitrifying group under each.

SUMMARY ON METHODS OF TESTING FIRE CLAYS

A survey of results of the various tests on Iowa fire clays seems at first to present some very discordant results. Some of the older and still frequently published statements as to the importance of chemical analysis, the effect upon fusibility of various minerals in a clay, the value of the empirical formula, etc., are not well supported by the results here given. In fact, the

TABLE X—THE RELATION OF ACTUAL FUSION POINT TO THAT CALCULATED FROM THE EMPIRICAL FORMULA[7]

CONE OF FUSION	MOLS. SILICA	MOLS. R. O.	CONES DIF.		CONE OF FUSION	MOLS. SILICA	MOLS. R. O.	CONES DIF.	
36	2.00	.074	0		..	2.67	.195	—1½	
35½	1.98	.101	½		31	3.42	.345	1	
..	1.84	.114	½	Ave.	30½	5.16	.364	2½	
35	2.07	.048	—1	2.080 SiO_2	..	3.03	.314	½	3.510
..	1.94	.040	—1½	0.080 R.O	30	1.91	.219	—3	0.258
..	2.06	.005	—2	1.000 Cones Dif.	29	1.68	.130	—6	2.200
..	1.93	.095	— ½		..	5.66	.196	—1	
..	2.02	.077	—1		28½	3.17	.419	— ½	
—35	2.87	.163	2		27	4.90	.145	—4	
34½	2.59	.088	½		34	2.14	.147	0	
34	1.99	.047	—2		..	1.95	.099	—1½	
..	2.50	.029	—2		33÷	1.04	.098	—4	
33	2.27	.091	—2	2.650	33	2.95	.123	0	
..	2.56	.244	1	0.140	32	3.35	.201	0	Ave.
32½	3.56	.207	1½	1.300	..	2.85	.114	—1	2.540
..	2.83	.206	½		31½	2.34	.144	—2½	0.144
31½	2.74	.109	—2½		..	3.17	.224	— ½	1.400
..	2.85	.239	— ½		..	2.46	.098	—2½	
					..	3.35	.153	— ½	
					31	2.39	.179	—3	

..	2.37	.198	—2		29½	3.72	.218	—1½	
..	2.62	.208	—1½		29	6.96	.121	—1	
..	2.07	.061	—5		..	2.48	.250	—3	
..	3.77	.186	— ½		..	4.40	.223	—1	
..	3.95	.202	0	3.470	28½	4.65	.277	—1½	4.090
..	3.87	.151	—1	0.165	28	3.19	.186	—4	0.217
..	2.29	.098	—4	1.600	27½	5.02	.331	—1½	3.200
..	3.27	.142	—2		26½	3.70	.181	—5½	
31	3.27	.203	—1		26	3.85	.220	—5	
30½	3.78	.218	— ½		25	4.41	.169	—6	
30	6.96	.099	0		24½	2.59	.217	—5½	

[1] The analyses and fusion points of the first group were obtained from *Geol. Survey of N. J.*, Vol. VI, *Iowa Geol. Survey*, Vol. XIV and *"Clays*, etc.," by Ries. The second group was obtained from the work of Bleininger and Brown in Vol. XIII, *Trans. Amer. Cer. Soc.*

work here presented shows that it is not possible to correlate the actual "standing up" qualities of a fire clay in actual service, with the chemical analysis. Some cases do, of course, occur where differences in durability under service condition can be traced to differences in chemical composition, but such cases are exceptions. The work of Rankin and Wright, published in the *American Journal of Science*, January, 1915, substantiates this viewpoint to a remarkable degree. Their results for the lime-silica-alumina mixtures proves conclusively that no rule can be adopted by which the fusion point of an untried mixture of those three components can be anticipated. It reasonably follows that similar results might be obtained for mixtures of any other three components, and that the greater the number of components the more complex the results. This is well supported by the findings in the present investigation.

What we are most concerned with in the use of a fire clay, is its ability to retain shape and rigidity under the conditions of use. Obviously, the conditions of use may vary somewhat, but we can almost always count on load and high temperature as being the two most important agencies for destruction. Hence, it follows that the best information concerning the quality of a fire clay can be obtained from those tests which measure the quality of rigidity under the conditions of either or both high temperature and load.

The tests which comply more or less closely with these conditions are the fusion test, porosity at varying heat treatments, rate and degree of warpage and the load test at high temperatures. The first, third and fourth have a direct application which is self evident. The fusion test, being the determination of the temperature of a condition at which the clay has passed its usefulness, is probably the least useful of the three. No direct relationship has been found to exist between fusion point and the quality of rigidity under the normal conditions of use. The rate and degree of warpage and the load test at high temperatures are somewhat analogous with respect to the conditions of the test but with this difference, that the load applied in the first is much

smaller in comparison. However, surprising as it may at first seem, there appears to be no relationship between the results of the two tests. Failure under load does not occur in the same order as failure in the warpage test of the same clays.

The determination of porosity is one method of measuring the rate and degree of vitrification. However, there is no relation between the rate of porosity decrease and the rate of warpage as is evident from Table XI following:

TABLE XI—THE RATE OF WARPAGE AS COMPARED WITH RATE OF SHRINKAGE AND POROSITY DECREASE

CLAY NUMBER	TOTAL WARPAGE AT CONE 11	WARPAGE PER CONE	POROSITY DECREASE PER CONE	SHRINKAGE PER CONE
	percent	*percent*	*percent*	*percent*
41	1.6	0.16	1.00	0.10
34	4.1	0.18	1.75	0.09
25	5.7	0.23	2.90	0.56
44	3.2	0.23	1.40	0.07
36	6.9	0.28	1.70	0.30
26	4.3	0.31	1.40	0.38
27	2.4	0.60	0.41	0.05
31	13.5	0.97	0.83	0.21
35	23.2	1.19	1.43	0.29
43	26.0	1.41	1.33	0.30

It is thus made evident that warpage or tendency to deform under load is not a function of the degree of vitrification as referred to clays in general. The tendency to deform depends upon the amount of viscosity of the fluid portion of the clay. The amount of the fluid portion of the clay and its viscosity change with increasing heat treatment and is peculiar to each individual clay. Thus it is, that different clays at the same stage of vitrification may exhibit different tendencies to deform. Hence, a measure of the progress of vitrification either by means of porosity determinations or in some other manner is not likely to measure with certainty the "standing up" qualities of a fire clay.

However, the present work has shown the porosity data to be of much value.

The test under load at high temperatures is the most directly applicable of any fire clay test thus far proposed. It has a direct bearing upon the quality of rigidity under conditions of use, and the results require no interpretation.

As has been pointed out earlier in this paper, refractories are used under a great variety of conditions, and for this reason the tests for clays to be used for a particular purpose should be selected and carried out with that purpose in mind. But for tests of fire clays in general, the load test, warpage, fusion point and porosity give all the necessary information.

DISCUSSION

Prof. Parmelee: Mr. Beecher has introduced us to a class of clays that seem to be rather unique. namely, non-vitrifying, non-refractory clays; I would like to ask Prof. Bleininger whether that is in line with any experience he has had with various clays?

Mr. Bleininger: Non-vitrifying and non-refractory?

Prof. Parmelee: That is the way I understood Mr. Beecher.

Mr. Bleininger: It seems to me that their non-refractory character might be determined in the load test; I would like to ask Mr. Beecher whether he included them?

Mr. Beecher: The term "refractory" I suppose should be defined for a proper understanding of the matter.

Prof. Parmelee: Mr. Beecher. as I recall it, clay No. 31 had a fusing point below cone 26?

Mr. Beecher: Yes sir.

Prof. Parmelee: And that was the one you referred to as a "non-vitrifying, non-refractory clay?"

Mr. Beecher: Yes, sir.

Mr. Bleininger: It is possible that the fluxes were present in the form of coarser mineral particles which especially in silic-

eous clays, would not promote vitrification and yet would cause the clay to soften at the temperature in question. I am not competent to give an opinion as to this case without further knowledge of the clay.

Mr. Beecher: I might add that this clay, No 31, was not particularly siliceous although it was a very short clay and seemed to be somewhat granular, but chemical analysis does not show an excessive amount of silica.

Prof. Parmelee: It probably passed through some state of vitrification before fusion?

Mr. Beecher: Yes, sir.

Prof. Parmelee: So that the term you apply is not strictly accurate?

Mr. Beecher: It is relative rather than accurate.

Prof. Parmelee: It seemed to me quite unique. I would like to ask Mr. Purdy whether he has any comments to make on the exceptions Mr. Beecher has pointed out; namely, that all clays found in the No. 1 fire clay area do not possess the characteristics of No. 1 fire clay?

Mr. Purdy: You will find clays that are exceptions to any rules laid down. The general rule I think is that refractory clays, refractory from the standpoint of fusion, will remain quite open and porous throughout the range described. I have seen no reason for abandoning the "rate of vitrification" basis of classification of fire clays. I have watched the data given by others who have investigated fire clays since my method of classification was published and can say with positiveness that this one clay, so far as I know, is the lone exception to the rule.

Mr. Beecher: In the use of the term "non-vitrifying" with reference to clay No. 31 it was not intended to imply that fusion of this clay takes place without going through a stage of vitrification. It would be hard to conceive of such a case. It was intended, instead, to be descriptive of the open and porous condition maintained between cones 1 and 11 which was very like that which we would expect in a non-vitrifying, refractory clay.

The porosity during this heat range was even higher than Purdy assigns as the upper limit for No. 1 fire clays. The action of this brick under the load test in which failure occurred without any evidence of vitrification or flowage, seems also to support the use of the term "non-vitrifying."

THE ROLE OF CHLORIDES IN THE VOLATILIZATION OF FERRIC IRON

BY GEO. A. BOLE AND R. M. HOWE, ALFRED, N. Y.

For many years, analysts have realized that ferric chloride could be volatilized from a concentrated solution containing this substance at the boiling temperature. Ceramists have taken advantage of the very low volatilization temperature of ferric iron in order to remove the color due to this element in certain white enamels.

The chlorine has commonly been supplied as sodium chloride, but not a little trouble has been experienced, due to blistering and the formation of gas bubbles in the enamel, owing to the incomplete driving off of the chloride. These difficulties having been met with at Alfred, it was deemed advisable to investigate the matter, with a view to the elimination, or at least the amelioration of the trouble.

One need only consult a table of the physical properties of the various chlorides to realize where a part of the difficulty lies. Common salt does not melt until a temperature of 813 deg. C. has been reached, and does not volatilize below a dull white heat.

The question arose, whether some chloride could not be used which would be as efficient as sodium chloride as a volatilizer of ferric iron, and that, when used in excess of the amount needed to drive off the iron, would itself volatilize or form a stable compound in the enamel by combining with the basic or acid constituents at a temperature below that at which the enamel matured.

With this in view, a variety of chlorides were chosen, some from a practical standpoint, and others because of a theoretical interest.

In order that all possible contingencies might be met, it was desirable to choose chlorides, first with a wide range of melting points and volatilizing temperatures, second, easily re-

ducible salts as well as very stable ones, and third, those with a relatively high percentage of chlorine and *vice versa*.

Accordingly, the chlorides of the following metals were used: sodium, potassium, lithium, barium, magnesium, lead, tin and silver.

A batch of tin enamel was made up with the following formula:

$$\left.\begin{matrix} K_2O\ .2 \\ CaO\ .3 \\ PbO\ .5 \end{matrix}\right\} \left.\begin{matrix} .25\ Al_2O_3 \\ .08\ Fe_2O_3 \end{matrix}\right\} \left.\begin{matrix} 2.8\ SiO_2 \\ 0.15\ SnO_2 \end{matrix}\right\}$$

This introduced 2.5 percent of Fe which was sufficient to leave a remainder in each case. The batch was divided into 50 gram portions, and into each lot, a known weight of a different chloride was introduced after the latter had been brought into aqueous solution, in order to insure a homogeneous mixture. The fusion was carried out in unglazed porcelain crucibles.

The enamel was then brought into a state of complete fusion in a large muffle kiln at cone 04. The burn lasted fifteen hours and the kiln was held at the temperature of fusion for five hours, after which it was allowed to cool with the dampers partially closed.

After many failures to secure consistent checks on the iron present after fusion, the following method was devised and gave excellent results when carried out with the greatest of care.

A sample from the center of the fusion was finely ground in an agate mortar till scarcely any grit was to be felt when ground between the teeth. The powder was introduced into a tall platinum crucible, and sulphuric acid was added. The crucible was then one-quarter filled with HF, and the silica driven off in the type of radiator devised by Hillebrand. The HF treatment was repeated, and the whole taken to dryness, or until the SO_3 fumes had just ceased to come off. The residue was digested for some time on the water bath, sulphuric acid added, and the whole treated with H_2S to reduce the iron. (This method was necessary in order not to reduce any of the other metals present, although it is much more tedious than many of the other procedures). The insoluble sulfates were filtered off. The H_2S was

boiled out in an atmosphere of CO_2, and the iron titrated under similar conditions, in order to avoid oxidation by the air. When this method was followed closely, a very sharp end point was obtained.

TABLE I

COMPOUND	BATCH	CHLORIDE ADDED	CHLORINE ADDED	CHLORINE ADDED	IRON AFTER FUSION	IRON VOLATILIZED	MELTING POINT	EFFICIENCY[1] FACTOR
	grams	*grams*	*grams*	*percent*	*percent*	*percent*	*degrees*	
$BaCl_2$	50	2.4935	.....	....	2.48	00.00	1059	00.00
NaCl	50	2.5784	1.509	2.87	2.23	10.08	813	3.76
KCl	50	2.7136	1.079	2.06	2.28	8.06	772	3.90
$MgCl_2$	50	2.2660	1.722	3.29	2.08	16.12	708	4.80
LiCl	50	2.1512	1.790	3.43	2.08	16.12	600	4.68
$PbCl_2$	30	2.1440	.5494	1.71	1.86	25.00	495	14.62
AgCl	50	2.3126	.494	.95	2.15	13.30	455	14.00
$SnCl_2$	50	2.4000	1.0140	1.92	1.60	35.48	249	18.47
Fe	..	2.5 int. as Fe	.....	....	2.48	.....	...	.....

[1] Efficiency factor is obtained by dividing the percent iron volatilized by the percent chlorine introduced as chloride.

The results in Table I are found to be in accord with the following theory: In the state of a homogeneous fusion, all the reacting substances are in a state of equilibrium. The amount of each compound formed in a given time depends on the temperature of the fusion, the concentration of the reacting substances, and the affinity constant for the given reaction. Liberally translated, the affinity constant means the tenacity with which the elements hold each other in chemical union.

In accord with this view of the situation, the iron would distribute itself among the more acid elements, in proportion to the affinity constants of the given reaction. If any one of these compounds so formed is volatile at the temperature of the fusion, it is evident that on passing off, it will destroy the equilibrium and as successive amounts pass off, the equilibrium will be displaced, in the direction of the volatile compound. If other substances were volatile at this temperature, they would also tend to pass off, but the preponderance of the reaction would be in favor of the most volatile constituent.

We are considering just such a system here. Ferric chloride is partially volatile at its temperature of formation (450 deg.) from the elements and to a less degree below this temperature.

In order that there be chlorine supplied, however, it is evident that the chloride introduced must have reached its melting point, or to have been so acted upon by the other constituents of the batch that it has been brought into fusion, or that it be volatile below its fusing temperature.

The latter premise is not true to an appreciable degree, in the case of any of the chlorides used. Therefore, we may safely postulate that there will be no volatilization of iron until the melting point of the introduced chloride is reached. If the percentage of iron volatilized is divided by the percentage of chlorine introduced as chloride, a factor results which we have chosen to term the efficiency factor. In other words, chlorine combined with different elements is a more efficient remover of iron in one case than in another.

If these efficiency factors are plotted against the melting points of the chlorides, it becomes evident that the higher the melting point of the chloride, the less efficient it is as a volatilizer of iron, *i. e.* barium chloride, with a melting point of 1059, had no effect, in this type of enamel, while tin chloride, with a melting point of 249, was the most efficient, the other chlorides varying in efficiency inversely as their melting points.

It was next attempted to make definite application of these results, obtained from a theoretical standpoint. Accordingly a batch of enamel was made up containing one percent of iron oxide by addition. To this, chlorides were added and the masses burned. Another enamel was made in which the tin was introduced as tin chloride. The results were very satisfactory. The tin chloride gave as good an enamel as the tin oxide and also eliminated the coloring influence of the one percent of iron oxide. Lithium chloride gave particularly good results. A fine color was secured, and the activity of the lithium as a flux was helpful to the structure of the frit, and the subsequent enamel.

The advantages of using tin chloride in preference to common salt are as follows:

Tin chloride is more efficient in volatilizing any iron that may be present.

Tin chloride is more completely decomposed at lower temperatures than sodium chloride. This eliminates trouble arising from soluble salts in the frit and also from the further decomposition of the salt during the glost burn.

Tin chloride does not volatilize in such a way as sodium chloride (salt-glazing process). This makes the accurate calculation of the formula possible, which is not true when salt is used in the batch.

The two sources of tin are equal in price per equivalent.

Thus tin chloride can be used as a valuable ingredient for the production of white enamel.

DISCUSSION

Mr. Bleininger: I think that this is a very pretty piece of work, and I am very grateful for such a contribution. I would like to ask, whether any one here who has dealt with iron enamels knows why European manufacturers introduce ammonium chloride?

Prof. Staley: I was very much interested in this paper and appreciate it very highly. I really never understood why ammonium chloride should be used in enamel and therefore am grateful for the information brought out by this research. I might say that there are a great many enamels used in this country in which no chloride is introduced, but these contain a large amount of fluoride. Chlorine and fluorine as we all know belong to the same chemical family, the group of chemical elements called the halogens, and their reactions are very similar. In this country the iron is volatilized as iron fluoride, in Germany it is volatilized, presumably, as the chloride.

THE VISCOSITY OF PORCELAIN BODIES[1]

A. V. BLEININGER AND C. S. KINNISON, PITTSBURGH, PA.

The present work is a continuation of the experiments reported in these *Transactions*, Vol. XV, p. 328, in which the elongation of porcelain bars, subjected to a tensile stress of five pounds per square inch, was studied in connection with variations in composition and at several temperatures. The shape of the specimen was different from the one used in the earlier study and is shown in Fig. 1. This test piece proved to be very satisfactory. The compositions of the porcelains thus studied were intended to include higher feldspar contents and have been compiled in

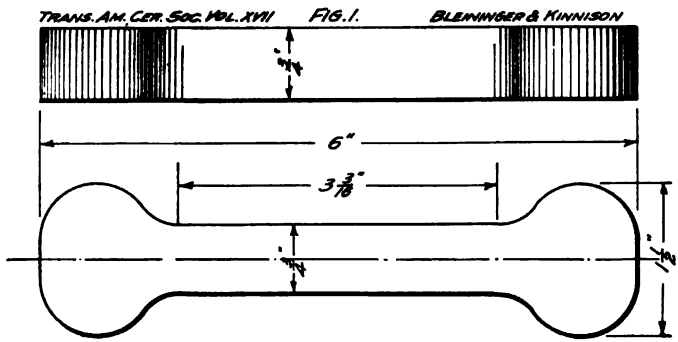


Table I. The clay content was made up of North Carolina kaolin, Georgia kaolin and Tennessee No. 3 ball clay in the ratios of 5:1:1. The feldspar used was an average grade of Maine potash spar, and was the same used in the previous work. The bodies were prepared by grinding wet in the ball mill and filter pressing. Plaster molds were used in pressing the specimens. After the pieces were dry, fine shrinkage marks were made on them, four inches apart. All of the specimens were first burned to cone 10. The fire-clay load pieces to be attached to the lower end of the specimens were made at first to weigh five pounds, but it was found that this weight was entirely inadequate, since

[1] By permission of the Director, Bureau of Standards.

no deformation was obtained. Burns were made then with pieces giving 7.5 and finally 14.5 pounds per square inch. This latter weight was adopted as the standard condition for this series. This shows clearly that the bodies previously studied, containing from 10 to 25 percent of feldspar, show far less resistance to deformation under tensile stress than the present series with higher feldspar contents. This would appear to be logical from the viscous nature of the feldspar. Several runs, made

TABLE I—COMPOSITION OF BODIES

NO.	CLAY	FELDSPAR	FLINT
	percent	*percent*	*percent*
1	35	30	35
2	35	40	25
3	35	50	15
4	35	60	5
5	35	65	..
6	40	30	30
7	40	40	20
8	40	50	10
9	40	60	..
10	45	30	25
11	45	35	20
12	45	40	15
13	45	50	5
14	45	55	..
15	50	30	20
16	50	40	10
17	50	45	5
18	50	50	..

below 1275°C., showed contraction; elongation due to softening was first observed at this temperature. It is quite probable that contraction and elongation practically neutralized each other within this temperature region. The pieces were hung from fire clay grids, the weight pieces attached and the kiln brought to the desired temperature at the rate of 30°C. per hour. All bodies were vitrified and non-absorbent. The lengthening of the pieces is expressed in terms of the length after the biscuit burn at cone 10.

Results. The results obtained are compiled in Table II, and for bodies No. 8 to 18 are shown graphically in Figs. 2, 3 and 4. In the 35 percent clay series, a number of pieces were found to be broken at the higher temperatures, indicating that, with low clay content, low tensile strengths are obtained. This is to be expected, since in the previous series a load of five pounds per square inch was sufficient to bring about decided deformation. The results, although incomplete, bring out quite clearly the fact,

TABLE II—ELONGATION MEASUREMENTS

NO.	BISCUIT LENGTH	LENGTH 1275°	LENGTH 1295°	LENGTH 1315° 1320°	LENGTH 1345° 1350°	LENGTH 1380°	ELONG. 1275°	ELONG. 1295°	ELONG. 1315° 1320°	ELONG. 1345° 1350°	ELONG. 1380°
							percent	*percent*	*percent*	*percent*	*percent*
1	2.56	2.56	2.56	2.62	2.66	Broke	0.0	0.0	2.3	3.9	...
2	2.56	2.57	2.59	2.62	Broke	....	0.4	1.2	2.3	...	...
3	2.48	2.48	2.49	2.50	2.54	Broke	0.0	0.4	0.8	2.4	...
4	2.51	2.51	2.53	Broke	....	....	0.0	0.8	...	...	...
5	2.51	2.51	2.53	2.55	Broke	....	0.0	0.8	1.6	...	...
6	2.50	2.50	2.51	2.51	2.51	2.55	0.0	0.4	0.4	0.4	2.0
7	2.49	2.49	2.50	2.51	2.51	2.54	0.0	0.4	0.8	0.8	2.0
8	2.48	2.48	2.49	2.50	2.50	2.52	0.0	0.4	0.8	0.8	1.6
9	2.50	2.50	2.52	2.54	2.54	2.56	0.0	0.8	1.6	1.6	2.4
10	2.46	2.46	2.48	2.48	2.48	2.49	0.0	0.8	0.8	0.8	1.2
11	2.49	2.49	2.50	2.50	2.50	2.54	0.0	0.4	0.4	0.4	2.0
12	2.46	2.46	2.48	2.49	2.49	2.51	0.0	0.8	1.2	1.2	2.0
13	2.44	2.44	2.45	2.45	2.45	2.47	0.0	0.4	0.4	0.4	1.2
14	2.46	2.46	2.47	2.49	2.49	2.50	0.0	0.4	1.2	1.2	1.6
15	2.45	2.45	2.46	2.46	2.46	2.48	0.0	0.4	0.4	0.4	1.2
16	2.44	2.44	2.45	2.46	2.46	2.47	0.0	0.4	0.8	0.8	1.2
17	2.43	2.43	2.45	2.45	2.45	2.46	0.0	0.8	0.8	0.8	1.2
18	2.44	2.44	2.45	2.45	2.45	2.46	0.0	0.4	0.4	0.4	0.8

that with low clay content, high percentages of feldspar are effective in reducing the rigidity or viscosity of the body. At the temperatures involved, such bodies are far more subject to deformation than those having a higher clay content.

From the observations upon the 40 percent clay series it appears that the greatest degree of softening is reached with 60 percent feldspar (no flint). The presence of flint increases the viscosity. Of bodies Nos. 6, 7 and 8, the ones containing 30 and

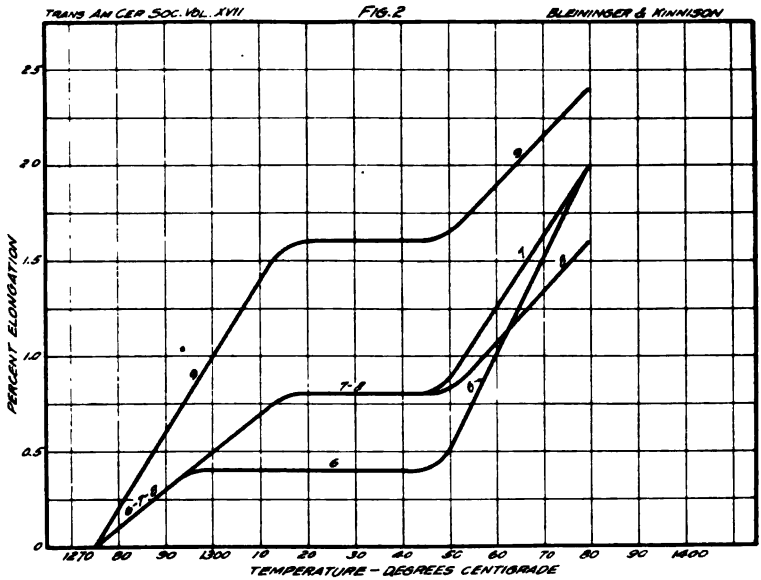
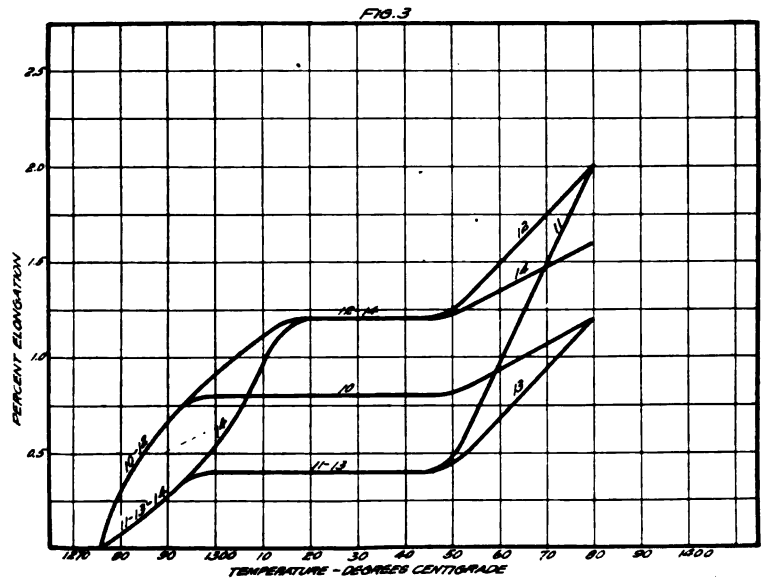
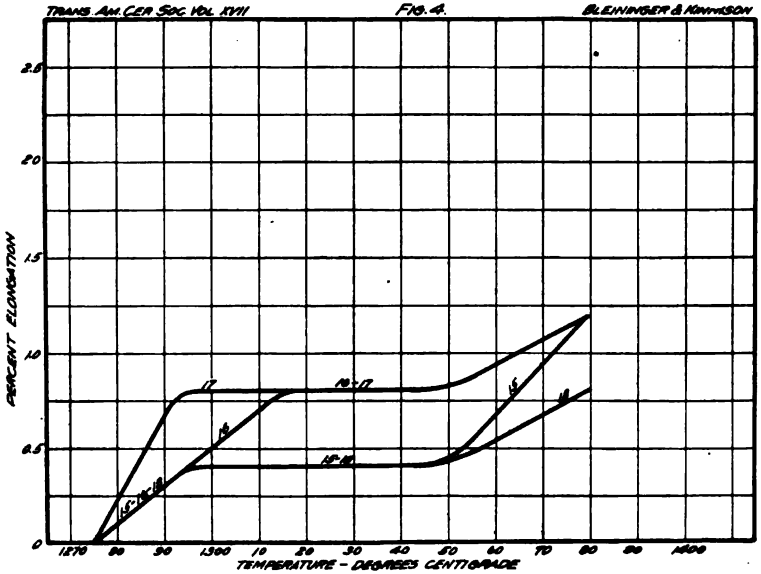

TRANS AM CER SOC. VOL. XVII
FIG. 2
BLEININGER & KINNISON
PERCENT ELONGATION
TEMPERATURE - DEGREES CENTIGRADE
2.5
2.0
1.5
1.0
0.5
0
1270
80
90
1300
10
20
30
40
50
60
70
80
90
1400
9
7
8
7-8
6
6-7-8

FIG. 3


PERCENT ELONGATION
TEMPERATURE - DEGREES CENTIGRADE
2.5
2.0
1.5
1.0
0.5
1270
80
90
1300
10
20
30
40
50
60
70
80
90
1400
12
11
14
12-14
10
13
10-12
11-13
11-13-14

40 percent of feldspar seem to reach about the same degree of viscosity at the maximum temperature. The greatest rigidity at the highest temperature seems to be shown with a feldspar content of 50 percent. At 1345°C., body No. 6, consisting of 30 percent feldspar and 30 percent flint, is most rigid. Of considerable interest in this set of curves is the fact that three distinct viscosity stages are recognized. At first, softening is observed which at from 1295 to 1315°C. changes to a state of rigidity, since no further elongation is noted. This conditions remains



constant up to 1345° from which point on a decided loss in rigidity is noted, and the elongation becomes quite marked. This would seem to indicate further solution of flint and clay by the feldspar, resulting in a viscous magma able to resist deformation. At 1345° the temperature, however, is sufficiently high to bring about softening of the entire mass. According to the viscosity attained between about 1300° and 1345° three classes of bodies may be recognized, comprised, respectively, of No. 6, Nos. 7 and 8, and No. 9. The first of these evidently is the most rigid, and the last is the least rigid within this temperature range.

In the 45 percent clay series, the lowest viscosity (greatest degree of softening) at the maximum temperature appears with 35 percent and 40 percent feldspar, the least with 30 percent and 50 percent. The body containing 55 percent of feldspar is in the intermediate position as far as this point is concerned. The greatest degree of early softening is shown by Nos. 12 and 14. The most rigid body up to cone 1345° is No. 11, and hence it would appear to be the safest as far as the deformation is concerned, within the temperature range indicated. The shorter zone of zero deformation increases is shown by Nos. 12 and 14. The three viscosity stages mentioned above are again noted in this series. Between about 1300° and 1345° three classes of bodies may be observed; namely, those of the minimum viscosity, Nos. 11 and 13; of intermediate viscosity, No. 10; and greatest viscosity, Nos. 12 and 14.

The far reaching effect of higher clay content is at once noted in the 50 percent clay series. At 1380° Nos. 15, 16 and 17 reach the greatest degree of softening corresponding to an elongation of 1.2 percent, which is very much less than the maximum value for the other series. The system, therefore, by the further addition of clay has become as a whole very much more rigid. The smaller degree of softening is shown by Nos. 15 and 18. The body containing 50 percent feldspar is decidedly more viscous than the others containing flint. These two bodies and No. 13 are the ones showing least deformation of the entire series of 18 bodies. We again note the three viscosity stages observed in the preceding series and two classes of bodies, Nos. 15, 18, and Nos. 16, 17.

Collecting the bodies showing the greatest rigidity or viscosity at 1345°, we have the following compositions:

NO.	CLAY	FELDSPAR	FLINT
	percent	*percent*	*percent*
6	40	30	30
11	45	35	20
13	45	50	5
15	50	30	20
18	50	50	..

Summary. Throughout these series, the effect of higher feldspar content was to increase viscosity in a very marked degree, especially in the case of the low clay bodies. This is shown by the comparisons of the elongation observed in the first paper published, using a load of 5 pounds per square inch, with that observed in the present work, employing a load of 14.5 pounds per square inch. Thus, a body with 40 percent clay and 25 percent feldspar and a load of five pounds per square inch, showed an elongation of 7.62 percent at 1310°, while one with 40 percent clay and 30 percent feldspar, with a load of 14.5 pounds per square inch, shows an elongation of only 0.8 percent at 1315°, indicating a viscosity about 11.8 times as great. A slight decrease in viscosity is noted in the 40 percent clay series when all of the flint is replaced by feldspar. With 45 percent clay, feldspar contents of 35 and 40 percent are most effective in decreasing the viscosity. Higher percentages again increase it. A still higher clay content causes the softening effect of the feldspar to diminish decidedly. Flint in such high feldspar bodies does not seem to be an important factor in governing the viscosity. The greatest rigidity is evidently due to the high clay content.

The function of viscosity is not a continuous one. After attaining a certain degree of softening, a well-defined rigid state ensues which does not tend to approach further softening until a temperature of 1345° has been reached. Beyond this point the third stage of decided softening is entered upon. Although showing the same degree of viscosity at 1388°, bodies may be divided into several classes, according to the degree of viscosity shown between about 1300° and 1345°, which seems to be the most useful criterion. High clay bodies having as the other constituent only feldspar, show very great viscosity. The most viscous bodies have been assembled.

The results should be of some service in the selection of bodies least subject to deformation in the firing process.

THE RELATIVE ACTION OF ACIDS ON ENAMEL

BY EMERSON P. POSTE

Upon looking into the matter of previous investigations relative to the action of acids on enamel, one finds that no great amount of research has been accomplished. We are indebted to some few investigators in Europe for contributions of interest, but the greater part of such data concerns the action of acids on glass.

In the Transactions of this Society, we find some very interesting records. The first definite set of tests mentioned is the Hooper tests, which, though having some very good points, are criticized as also having objectionable features. In Volume XI of the Transactions Professor Orton reports a series of tests on automobile licenses. He was able to make a definite decision as to the quality of the material being tested, but by expressing the results of his acid tests in percent loss, rather than loss per unit area,—perhaps failed to draw as definite conclusions as his work made possible. Professor Orton closes his paper with an appeal for research leading to the establishment of a standard test for acid resisting qualities of enamel.

In Volume XII, J. B. Shaw records work along this line, resulting from Professor Orton's suggestions. He figures his data to loss of weight per unit area under standard conditions, which would seem to be a very necessary feature. He then proposes a test which he holds to be a satisfactory means of determining the relative acid resistance of enamels. How generally this test has been adopted, we have not been able to ascertain.

In Volume XIII, R. D. Landrum gives a very interesting report of his tests, using various initial strengths of acetic acid which he boils to dryness in a weighed enameled test dish. From his data, he plots a curve on acid strength against loss in weight. His tests, no doubt, offer a rapid method for obtaining in a general way, the desired results, but owing to constant change in acid strength he has a complex condition which, of course, must have a very definite bearing on the solubility curve.

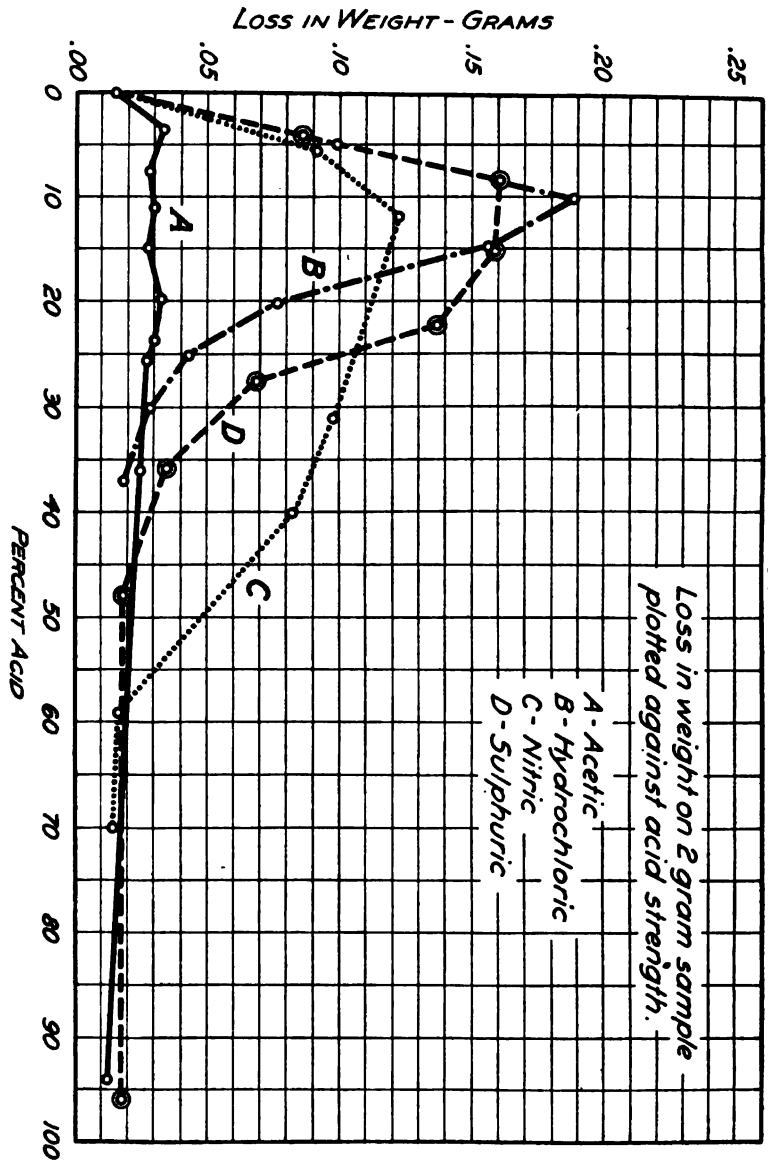
These investigations, the last named in particular, caused us to become interested in the nature of the attack of acid upon enamel, and the relative action of different acids on a given enamel. It is quite evident from data previously noted that the dilute acetic acid is more corrosive than the stronger solutions. What is the case for other acids?

Object. From the above it is seen that the object in devising a means of comparing the action of acids on enamel was to determine the relative action produced when an enamel is exposed to different strengths of the same acid, to compare the various acids as to their relative action, and to study the nature of the action of acids on enamel.

The method of using a small test dish coated with the standard enamel was not used for two reasons. First, the standard enamel used was of a type having acid resisting qualities such that, within a reasonable time, no appreciable loss could be obtained without exposing a very large surface of the enamel to the liquid, thus taking the investigation beyond the range of the analytical balance. And secondly, this type of enamel is not at its best when used on thin material such as would be used for small test dishes. So the problem was that of exposing to the liquid to be tested, a large surface of enamel without introducing the objectionable features of large test dishes, or smaller ones on which the enamel would not be at its best.

Method. A scheme which has proven very satisfactory is to place a small amount of finely powdered frit in a definite amount of the acid to be used. After allowing the test to stand for a definite time, the remaining frit is recovered on a weighed gooch crucible with asbestos filter, and the loss of weight determined.

In carrying out the work the greatest care has been used to keep conditions constant. Two grams of the standard frit have been weighed into a 400 cc. beaker, 100 cc. of the acid added, contents of beaker thoroughly stirred, covered with a watch glass, and allowed to stand twenty-four hours at laboratory temperature, which was known to be practically constant. After filtering, the crucible and residue were dried on a warm hot-plate.


LOSS IN WEIGHT - GRAMS
.00
.05
.10
.15
.20
.25
0
10
20
30
40
50
60
70
80
90
100
PERCENT ACID
A
B
C
D
Loss in weight on 2 gram sample plotted against acid strength.
A - Acetic
B - Hydrochloric
C - Nitric
D - Sulphuric
TRANS. AM. CER. SOC. VOL. XVII
FIG. 1.
POSTE

In the selection of a frit for this work, one was chosen which, when used as an enamel, was known to have fairly good acid-resisting qualities, but, however, did not have a particularly high acid resistance. The frit was pulverized dry in a laboratory pebble mill, and that which passed through a fifty mesh sieve was taken. The powder so obtained when tested on standard cement sieves, gave the following results:

Passed through 50 mesh, retained on 100 mesh 4.90 percent. Passed through 100 mesh, retained on 200 mesh 33.90 percent. Passed through 200 mesh, 61.2 percent.

Chemically pure acids were used, diluted with distilled water, the strength of the dilute acid being determined by titrating with standard alkali.

The question of possible experimental errors was investigated. Assuming the treatment of the frit to be constant up to the time of filtration, which was, no doubt, reasonably certain, the possibilities for errors due to different thicknesses of asbestos and different rates of filtration were investigated. It was found that constant results could be obtained, using the same strength of acid through much wider ranges of variation in the above details than would obtain in actual work. Hence, it seems safe to neglect these possibilities for error.

Data. The results of these tests can be most clearly shown by plotting the loss of weight on a two gram sample of standard frit against acid strength. Figure 1 shows such curves for hydrochloric, nitric, sulphuric and acetic acids, while Figure 2 shows again the curve for acetic acid, together with curves for the same acid, as obtained by Landrum. A comparison of these curves will follow. Figure 3 shows the results of a series of tests, using a constant strength of acid (ten percent hydrochloric), but allowing the tests to extend over varying periods of time.

To note the effect of the difference of size of the particles of frit, a series of tests was run, using in each case two grams of powdered frit as follows:

(**A**) Particles passed through 50 mesh, retained on 100 mesh. (**B**) Particles passed through 100 mesh, retained on 200. (**C**)

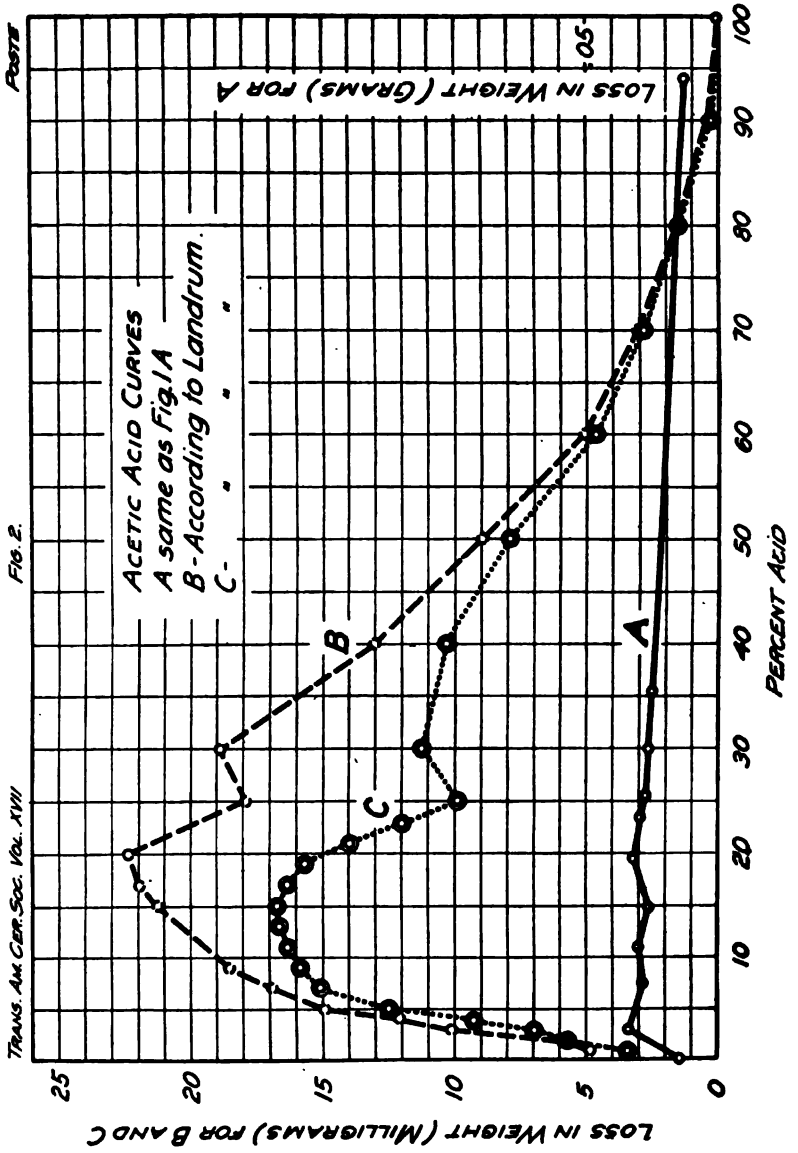


Fig. 2.

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Paste

Particles passed through 200 mesh sieve. The resulting losses of weight under the standard conditions, outlined above, using twelve percent hydrochloric acid, were

(**A**) .0522 grams. (**B**) .0926 grams. (**C**) .2329 grams.

In connection with this data there are several points of interest. First of all, the general shape of the curves in Figure 1 is quite consistent with the ideas advanced in the discussion of Mr. Landrum's previous work. The more dilute acids become more active to a certain maximum, beyond which point further dilution decreases the activity. This has been attributed to the fact that the greater the dilution the greater the dissociation. This fact cannot be disputed though it does not, as stated, account for the maxima observed. It seems quite logical to assume that the action bears some definite relation to the ion concentration. Diluting the acid produces increased ionization and greater ion concentration to a certain point, beyond which the addition of more water, though still increasing the percentage ionization, decreases the actual ion concentration. It would be interesting to compare these curves, with curves for ion concentration for these acids, but such data does not seem to be available.

It will be noted that at the zero end of the acid strength scale the solubility was about .015 in all cases. This figure is obtained by using distilled water and either represents the action of water on the powder, or a constant experimental error, or a combination of the two. It is known that pure distilled water has a more corrosive action on glass than is the case for very dilute acids, but the acid dilution was not carried low enough to enable us to observe that feature in connection with the work being discussed.

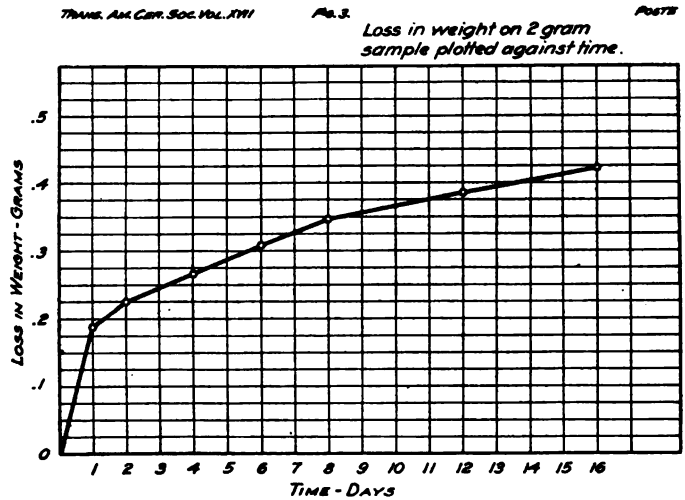
The relative action of acetic acid compared with mineral acids is very clearly shown on Figure 1.

Interest in Figure 2 centers about two features. First—Landrum's curves show a marked irregularity at 25 percent acetic acid; with this in view tests were made for small differences in concentration to a point well beyond this, but no such irregularity was noted. Secondly—the flatness of curve **A** as compared with **B** and **C** would seem to indicate the general dif-

ference of acid resisting quality of the enamels. The increased activity of the diluted acid produced a marked effect on the ordinary enamels but produced only a very slight effect on the acid resisting enamel used.

Figure 3 indicates the effect of time of exposure, but the data does not have a great bearing on the tests further than to indicate the effect produced by not keeping the time constant.

The importance of considering the area of the surfaces exposed is very clearly shown by the results of the tests on different sized particles. In each case, the same amount of enamel



was used, and the only difference was in the size of the individual particles. The results expressed in percentage lost are **A**—2.61 percent; **B**—4.63 and **C**—11.65. This is conclusive evidence that any test of the action of an acid on an enamel must take into account the area of the surface exposed.

Conclusion. We hope that the work reported here may be the forerunner of further research. A study of the action of acids on enamel at a single temperature is, at best, but a start. We plan to modify these tests so as to be able to get corresponding data for different temperatures of acids, including boiling solutions. Some preliminary work along this line has already

been accomplished, but the results to date would be a more profitable consideration in connection with the results which we hope may follow, than would be the case, should they be considered with the above data.

In conclusion we may state that we do not, at present, at least, claim for the above scheme of investigation any merits as a means of comparing enamels as to acid resistance. No doubt the preparation of absolutely uniform samples from various frits would present serious difficulties. But we do think that we have been able to throw some light on the nature of the action of acids on an enamel, and to devise a method for determining the relative action of various acids on a given enamel. The method is clearly applicable to any solutions which one might desire to test, assuming the absence of material which would be held on the filter, or would have an appreciable action on the asbestos or the crucible itself.

DISCUSSION

Prof. Staley: I had the pleasure of having a copy of this paper sent to me before the meeting, that I might prepare a discussion. I have prepared Figures 4 and 5 and I would like to show them in connection with Figure 1.

These charts have to do with the dilution, or the ionic concentration, of the acids, when compared with practical results as derived by Mr. Poste. Along the abscissa in Figures 4 and 5, we have given the composition of the various acids shown. As ordinates we have the ionic concentration as measured by the conductivity of the solution. The electrical conductivity of a solution is, of course, proportional to the ionic concentration, or, in other words, the conductivity is proportional to the strength of the acid. I might say that the conductivity of the sulphuric, nitric and hydrochloric acids are shown on the same scale, but that for acetic acid is drawn on this scale multiplied by ten, that is, the conductivity of the acetic acid is represented as being just ten times as large as it should be, simply because it would not show on the drawing if reduced to its proper scale.

In a general way, there is a remarkable correspondence between the curves showing the strength of the acid and those

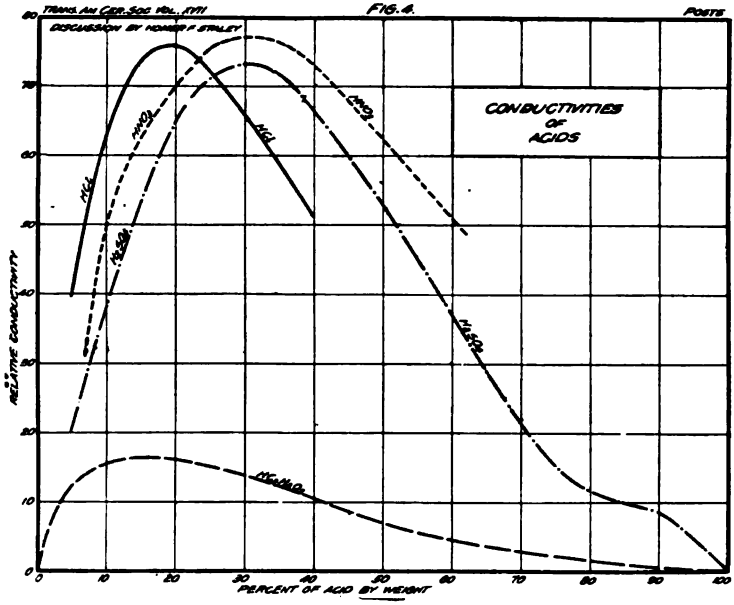

TRANS. AM CER. SOC. VOL. XVII
DISCUSSION BY HOMER F. STALEY
CONDUCTIVITIES OF ACIDS
HCl
HNO3
H2SO4
CH3COOH
H3PO4
RELATIVE CONDUCTIVITY
PERCENT OF ACID BY WEIGHT

FIG. 4.

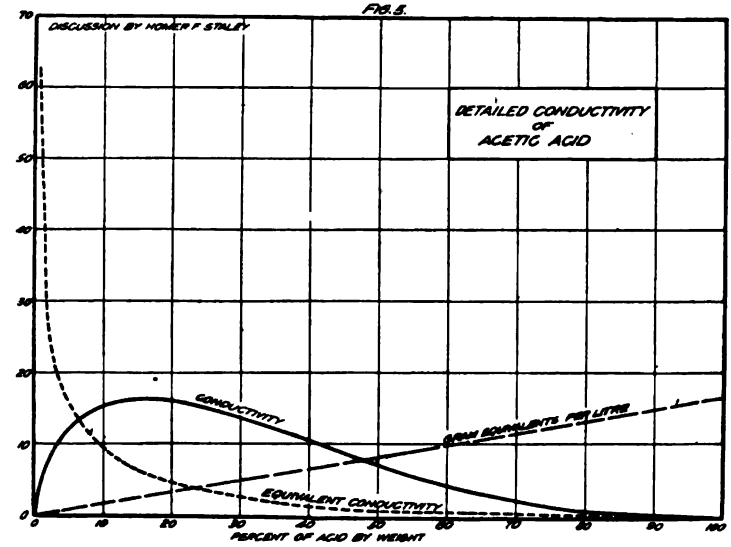

DISCUSSION BY HOMER F. STALEY
DETAILED CONDUCTIVITY OF ACETIC ACID
CONDUCTIVITY
GRAM EQUIVALENTS PER LITRE
EQUIVALENT CONDUCTIVITY
PERCENT OF ACID BY WEIGHT

FIG. 5.

showing the solubility of the enamels. We would not expect the curves to be identical for several reasons. One of these is that some of these acids form insoluble compounds with ingredients of the enamel, and these tend to cover the grain of the enamel with an insoluble coating which would modify the action of the acid. Lead sulphates, for instance, are more or less insoluble. Furthermore, just as soon as the acids start to act on the enamel, salts are formed, but because the strength of the remaining acid is decreased, due to the presence of its own salts in solution. These curves give the conductivity of the acids alone, but not the conductivity, or strength, of the acids in the presence of their own salts.

As to why the curves take the shape they do, I will discuss in relation to the figure. I submitted a statement of the general shape of the curve representing variation of strength of any acid with dilution, in a discussion of Mr. Landrum's paper, in Volume XIII, *Trans. Amer. Cer. Soc.*, but Figures 4 and 5 probably make the matter a little clearer. On the abscissa is shown the composition of acid. The ordinates from the dotted line represent the equivalent conductivity. It is the amount of electricity which is conducted by each molecule, or each ion of hydrogen which is present in the acid. It tells, in other words, the strength of each part of the acid you have present in the solution. The ordinates from the dashed line represent the gram-equivalents of acid per liter. If the number of parts of acid in a solution is multiplied by the strength of one part of acid in the solution, you obtain the strength of the total acid solution. Thus at any concentration of acid, the ordinates for the solid line showing the total conductivity of the acid solution as a whole, are found by multiplying together the ordinates from the two other lines.

Mr. Landrum's curve shows that starting with a given volume of acetic acid solutions of various strengths and evaporating to dryness, the greatest solvent action was shown by a solution containing from 15 to 20 percent acid by volume. Since the specific gravity (1.05) of acetic acid is so close to that of water, there is little difference in solutions of this acid between percentages by volume and by weight. Mr. Poste also found that the

highest solubility of the enamel in acetic acid was in solutions of 15 to 20 percent and this curve shows that the highest conductivity, or highest strength, of the acid comes between 15 and 20 percent of acetic acid.

With the method of testing enamels in grains, it would seem to me that it would be better to take grains which pass through one sieve and rest on another, than to take grains which pass through a certain sieve. The solubility will vary with size of grain, and size of grain may vary considerably when only one sieve is used.

If it is desired to have the same amount of surface exposed, in comparing different enamels, with the same size of grain, it is hardly safe to take a given weight. Enamels will differ quite materially in specific gravity, if the composition varies much. In fact, I have seen a difference in specific gravity of 20 percent. With the same size of grain and a fixed weight of any two powders, the surface varies inversely as the specific gravities. If it is necessary to test two enamels of different densities, the most exact method would be to take weights in proportion to their specific gravities.

Mr. Bole: Could not one simply look up the ionization constants of any of these acids and predict the corrosive reaction on any enamel?

Prof. Staley: You cannot find an ionization constant for an acid that will hold true over a wide range of concentrations. The curves given here are drawn from actual, experimentally determined results, and you cannot draw any one of these curves by a mathematical formula.

Mr. Bole: But you can approach very near to it?

Prof. Staley: If you use the ionization formula as given for dilute solutions, it will not apply at all for concentrated solutions.

Mr. Bole: Where you have no ionization you have no effect?

Prof. Staley: That is true. A curve drawn from an ionization constant would hold in a very general way, but no formula would give the curve shown here.

Mr. Landrum: Mr. Poste will find that his method will not give him the results that he anticipates, due to two reasons: His enamel, as tested, has only been melted once, and it has been quenched very quickly and subsequently powdered, and it is made up of surfaces which are easily affected by the acid. The finished tank would have the enamel fused the second time, and cooled very slowly. I have tried in making tests to use the powdered enamel, and did not get the same comparative results that I did in making tests on the ware itself. I think it is due to the surface action of these enamels. The relative acid-resistance of the fused surface cannot be judged from the acid resistance of the powdered enamel.

Mr. Poste: As to the point that Mr. Landrum makes, in connection with the test on common ware, what I wanted to do, was to find out if there was this maximum activity, and to be able to predict, whether for instance 30 percent sulphuric acid would be harder to handle than 10 percent.

Mr. Landrum: The paper would be worth a great deal more if Mr. Poste could give us an idea of the composition of the enamel. If he could give the specific gravity, as well as the fineness of grinding, it would help us make some calculation in regard to the surface attacked.

Mr. Poste: I am afraid I will have to handle these points myself.

DISCUSSION WRITTEN AFTER READING THE PAPER

Mr. Shaw: The method of testing used by Mr. Poste is undoubtedly the most accurate method yet proposed for determining the relative solubility of enamels in acids, but it is doubtful if it has any practical value. When enamel is put on sheet iron, it is almost invariably composed of frit plus clay and generally other materials such as opacifiers and tempering agents, all of which very greatly influence the power of the ware to resist acids. The resistance of the ware to attack by acids is also greatly influenced by the degree to which the enamel is burned on the ware.

The writer was at one time called to make a white acid-proof enamel. It was especially necessary that the enamel should re-

sist attack by strong lemon juice, which contains about seven percent citric acid. No one can realize the difficulty of making such an enamel except those who have tried to do so. Such an enamel will contain no fluoride, no lead, very little boracic acid, and yet must melt at enameling temperatures and produce white ware. The clue to the solution of the problem was gotten from Prof. Orton's paper entitled "An Easily Fusible Glass Without the Use of Lead or Boracic Acid." Citric acid is very much more effective in attacking enamels than acetic acid. In fact, it seems to the writer that it is the ideal acid for culling out the acid proof from the so-called "acid proof" enamel ware. It is the writer's opinion that an acid-proof frit will not necessarily produce acid-proof ware, although obviously the frit must be acid proof if the ware is to be so.

If the enamel is to be dusted on the ware, in which case nothing is added to the frit, then the method proposed by Mr. Poste will serve very well for the manufacturer in studying his enamels and improving his product, but it can not be used in classifying enamel ware.

Enamel ware may be conveniently divided into three classes, viz.: 1. Cast-iron ware which must be burned at low temperatures and if to be white is most difficult of all to make highly resistant to acids. 2. Thin sheet-iron enamel ware which can be burned at moderately high temperatures if colored, but if white the temperature of burning is very limited. In the former case, it is not difficult to make the ware highly resistant to acids, but in the latter case the difficulty is greatly increased. 3. Heavy steel or wrought iron ware, generally colored and easily made highly resistant to acids.

Mr. Poste: I am very grateful for the many valuable suggestions brought out in the discussion. No doubt it would be advisable to use sized particles passing some definite mesh and retained on a finer one. With different enamels being compared, the specific gravity as affecting the area of surface should be considered. Further, the tests on the frit are not as desirable as on the enamel fired on the ware, but I do feel that I have been able to carry out my original purpose in comparing the relative action of the different solutions on the given enamel at hand.

THE BUREAU OF STANDARDS CONTRAST METHOD FOR MEASURING TRANSPARENCY[1]

BY IRWIN G. PRIEST, WASHINGTON, D. C.

If, in a diffusely lighted space a black and white figure such as Fig. 1 be covered with a sheet of translucent material such as tracing cloth in contact with the figure, the important optical result is a reduction of contrast. The black becomes gray and the white becomes less bright. This net result is the joint effect of two actions of the translucent material, *viz*: its reflection of light and its absorption. It seems obvious, however, that this very net result is the thing of prime interest to the draftsman. It therefore appears reasonable to grade the transparency of tracing cloth by a measurement of this reduction of contrast. Having covered Figure 1 with a piece of tracing cloth, we might, *e. g.*, with a suitable photometer, measure the ratio of the brightness of the spot B to the brightness of the spot W. The value of this ratio will vary between zero and unity, being low for very transparent cloths and higher for less transparent ones. Anyone wishing to specify quantitatively the "transparency" of tracing cloth might accomplish his purpose by specifying a value of this ratio.

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[1] Published by permission of U. S. Bureau of Standards.

[1] The fundamental principle of this method was employed by Sammet in 1912, but his apparatus was rather imperfect. (C. Frank Sammet, A Measurement of the Translucency of Papers, *Bureau of Chemistry Circular No. 96.*) Messrs. E. D. Tillyer and Carl W. Keuffel at the Bureau of Standards used the same principle (April, 1913) by means of the Martens Photometer and improvised apparatus. A few months later (Summer of 1913), Mr. Priest, not knowing of the experiments of Tillyer and Keuffel, devised apparatus similar to theirs, but somewhat improved in convenience. Since then Messrs. P. V. Wells and C. G. Peters have been associated with Mr. Priest in developing, testing and improving the method and apparatus. It has been used in regular testing for more than a year. After the foregoing note was written, Mr. Priest, stopping in Rochester en route to Detroit, learned that Dr. Nutting was using the same method to test the transparency of translucent envelope windows, except that he was using for black a piece of very mat black paper which he said was equal to the black hole. Dr. Nutting is about to publish a paper treating the theory of this subject and was kind enough to outline informally, certain points of it during the visit just mentioned.

In describing this method to the Ceramic Society, the author does not wish to be understood as advocating its adoption. In the oral presentation he emphasized that he wished, by discussion, to find out the ceramist's purpose in measuring translucency and obtain his viewpoint. While this method is obviously a good one for tracing cloth he is of the opinion that another method may be found more suitable for the ceramist's purposes.

However, the specification would be of little value because the conditions of measurement would not be readily and certainly reproducible. Another piece of white paper might not be so white; another ink spot might not be so black. Our problem then is to choose and define a reproducible black and white. It will also be desirable to specify to a rough approximation the conditions of illumination.

As standard white, we choose a surface of magnesium oxide.[2]

As standard black, we chose a black acetylene smoke surface in the bottom of a black lined cavity into which we look through a hole in one side.

The observed surface of the sample is illuminated by diffused light from all directions above, care being taken to have the illumination over the black equal to that over the white.

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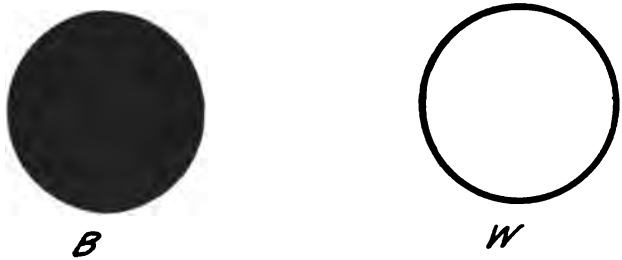
FIG. 1.



DESCRIPTION OF APPARATUS

The Photometer. The ratio of brightness is measured by means of the Martens photometer. A section of this instrument in the line of sight is shown in Fig. 2. *O* is a lens. *W* is a Wollaston prism. *Z* is a bi-prism. *N* is a nicol prism capable of rotation about its long axis. *J* is an index attached to *N*. *K* is a circle divided in degrees. On it angles of rotation of *N* may be read. *L* is a lens. *H* is the ocular for focusing on the edge of *W*. For complete theory of the instrument the original paper by Martens must be consulted.[3]

[2] Prepared by deposit of the "smoke" from burning magnesium ribbon. In this way a beautiful clean smooth reproducible mat white surface is easily obtained. The deposit should be made so thick that an increase in thickness does not increase its brightness.

[3] *Phy. Z's.* I, 299, (1900).

Suffice it here to say:

(a) One sees on looking into the photometer, a divided photometric field one-half of which is illuminated by light coming from *a*, while the other half is illuminated by light coming from *b*.

(b) The field can be "matched," *i. e.* the two halves brought to equality of brightness by turning the nicol.

(c) The ratio of the brightness of a surface sending light into the photometer along *a* to the brightness of a surface sending light in along *b* can be computed as a function of angles read on *K* when the photometric field is matched.

The Complete Apparatus. The complete apparatus is shown in Fig. 3. It is shown with line of sight, *AB*, horizontal. However, the apparatus may be turned about axis *CD* to bring the line of sight to any desired angle.

EFGH is a white lined box. *KL* is the standard white surface. *MN* is the black cavity. *1, 2, 3, 4, 5, and 6* are lamps. *OQ, RS* are diffusion screens. If paper is being examined, the sample is placed in the clip *TU*. If a plate of glass is being examined, the sample *XY* is placed in the slide *HZ*. The slide, as well as the clip, may be slid in and out from the top of the box. *VW* is the photometer; *I* and *J* are black spots to prevent direct reflection of light from the sample into the photometer. *C* and *D* are supports.

Ventilation of lamp boxes is provided by holes in top and bottom screened so as not to let light through.

The photometer may be rotated about the axis *AB* so as to reverse the field, and stops are provided 180° apart.

METHOD OF MEASUREMENT

The illumination of the surface covering the black hole must equal that of the surface covering the standard white. This is tested as follows:

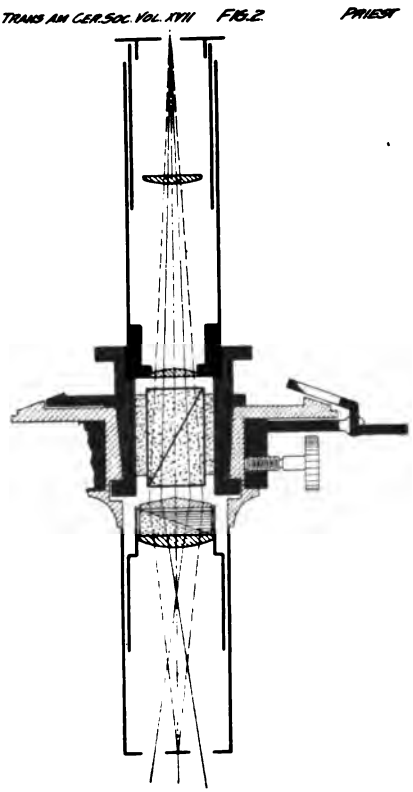
(a) Both the hole and the white surface are covered by a uniform opaque mat white plate.

(b) The photometer is turned so that one-half the field is illuminated by light from the part of the white plate over the

hole while the other half is illuminated by the part over the standard white.

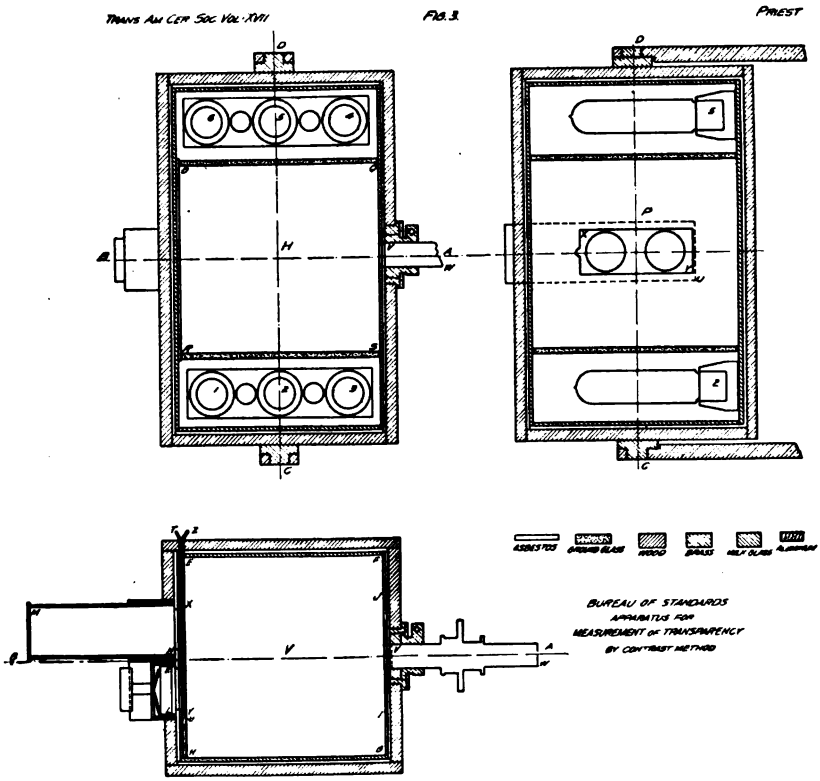
(c) The photometric field is matched.

(d) The whole photometer is turned about AB through 180°. If the condition of equal illumination is satisfied, the field will still be matched.



The sample is placed in the clip TU, so that part of it covers the black hole and part of it the white surface. The photometer is set so that the light from the part over the black hole illuminates the half of the photometric field which is extinguished for the position of the nicol which reads zero on the circle K. The photometric field is matched by turning the nicol

N. The angle θ_1 is read. (Index J on circle K). The photometer is rotated through 180° about axis AB. The photometric field is again matched and corresponding angle θ_2 is read.



Then,

$$\frac{B}{W} = cot\ \theta_1\ tan\ \theta_2$$

where B=brightness over the black hole
and W=brightness over the white spot.*

* Some months ago while the author was attempting to formulate a system of nomenclature for this subject he tentatively adopted the term "contrast ratio" as a name for the ratio B/W, and used it in laboratory records, intending, however, not to use it in any publication until more time had been given to the task of formulating a complete and consistent nomenclature. On visiting the Kodak Park Laboratory, Feb. 14, he was pleasantly surprised to find Dr. Nutting independently using this identical term as a name for the same ratio, (or its reciprocal?).

ACCURACY

Precision. The accidental uncertainty is, under the best conditions, less than one percent.

Reproducibility. (a) The results do not depend upon the exact amount nor upon the exact degree of diffusion of the illumination. The white lined box is merely a convenience, its exact reproduction is not a part of the specification.

(b) It is not necessary to use the Martens photometer. Check results have been obtained using the Beckstein photometer, an instrument entirely different from the Martens in principle and construction.

(c) The reproducibility of the magnesia surfaces within the uncertainty of observation has been demonstrated by repeated trials.

(d) The constancy of the same film for several days has been experimentally demonstrated.[5]

It is expected that more detailed data on this subject will be published later by the Bureau of Standards.

DISCUSSION

Mr. Bleininger: In measuring the translucency of our ceramic bodies, say for instance a porcelain plate, the question of thickness is involved. In previous work done and reported in the Transactions of this Society, it is assumed that the relation between translucency and thickness is a linear one. This has never seemed right to me, and I would like to ask Mr. Priest if he does not think this relation an exponential one?

Mr. Priest: Yes. If we have a plate of unit thickness, and the brightness of the first surface is I_o, while the illumination of the second surface received from the first is I_1, we have $\frac{I_1}{I_o}=a$, the transmission coefficient. Now if we take a plate of any thickness t and let I_t be the illumination of the second surface, we have $\frac{I_t}{I_o}=a^t$, which is the exponential law in question. It is

[5] It had been observed by Nutting and Jones, (*Trans. Ill. Eng. Soc.*, Vol. 9, p. 596), that the reflecting power of freshly calcined magnesia decreased 2 or 3 percent in a day or a few days. Experiment has shown that this is not true of our films.

assumed that the area of the plate is very large compared with the thickness and that the photometric observations are made in the center.

Mr. Stover: It may be alright to figure that way on a material that is of constant composition. But, for such determinations on china plates, you could use a micrometer to determine the thickness of the standard plate and of the plate being tested, and by comparison of the thicknesses and also of the compositions you could decide what was wanted. With tracing cloth, the standard test methods may be accurate, but until we standardize pottery as regards composition such standard tests will not get us a great ways.

Mr. Priest: What is it that you are particularly interested in, or are you interested in both things? Do you want to take a particular specimen of porcelain and get the ratio of transmitted to incident light for that particular specimen, or are you more particularly interested in grading materials? Do you want a constant that characterizes a material rather than a ratio which characterizes a particular thing?

Mr. Stover: Almost every potter uses from six to a dozen kinds of clay in his mix for the development of other properties than translucency. Only within the past twenty years have the potters been producing anything but opaque ware. Now a few are making beautiful translucent thin ware, and a few are making bone china. It would be an elegant thing to set a standard so that a potter might say "we have a No. 2 translucency in our body." But who shall establish the No. 1 standard?

Mr. Priest: Don't say No. 2 and No. 1, but adopt your nomenclature in terms of incident and transmitted light. This very question came up with the American Optical Company a few weeks ago. They asked our advice as to the grading not of translucency, but of transparency of glasses. They make a series of smoked glasses of increasing density, some very thinly smoked and some very dense, so that you cannot see through them very well. They wanted to know how to grade these. At present they grade them arbitrarily 1, 2, 3, or A B C, or they grade them X Y Z, or a, β, γ, *etcetera*. Now they import these glasses,

and the American Optical Co. complained that the glasses they get from abroad are not consistent, that is, one No. 2 corresponds to another marked No. 1. It seemed to me that the first step in straightening out these inconsistencies was to adopt a rational instead of a purely arbitrary nomenclature, so I suggested that they grade their glasses by percentage transmission. Consider a plate of glass, with a beam of light incident on it, a fraction of which is transmitted. You can measure the ratio of the intensity of the transmitted light to the intensity of the incident light. Where there is no scattering, no diffusion, it is simply a question of relative candle power. Say one plate transmits 10 percent, one 20 percent another 30 percent, *etcetera.* Then label the plates accordingly. A plate that transmits 10 percent, mark 10 percent on it; one that transmits 20 percent, mark 20 percent on it, and so on. You say "This has got to be done in a rapid manner, just by casual observation, we cannot go by the photometer." All right; a man can look at a standard marked 10 percent, and compare another glass with it, and he can look at a standard marked 20 percent and compare a glass with that, and when he has graded in terms of percent transmission instead of in terms of A, *etcetera,* though he has not obtained the highest photometric precision, he has a nomenclature that can be checked up with that precision.

Mr. Stover: When you talk in percents, you will be understood by most of the people, but when you use scientific terms in comparing properties of pottery, you will not be understood. There are in our Society, a great many potters that have quite a reputation for what they have accomplished, but they will not even stop to read a technical article, though it might pay them right well to do it.

Mr. Priest: I don't want to pretend to tell the potters how to do it; in fact, I tried to make clear at first that may main purpose was to try to ascertain what you wanted done. We have heard from Prof. Bleininger and others, that you want to do something in the measurement of translucency. If I can find out at this meeting what you want to do, it will help us very much to do it.

Mr. Jackson: I should like to ask Mr. Priest one or two questions. I am very much interested in what you have described here; I believe it is of great value. I think you are leading us in the right direction, and there is no use trying to stop the procession in any way. I think we had better learn, as rapidly as we can. Now I would like to know how you are going to measure the translucency of a plate with the apparatus that you have described? I don't believe it is possible, is it?

Mr. Priest: What kind of a plate?

Mr. Jackson: An ordinary dinner plate.

Mr. Priest: I could not do so, mechanically, because I could not get it into the apparatus; I would have to break it; that is a matter of mechanics and convenience. This whole box is a convenience. It was designed primarily for measuring tracing cloth. I can put rectangular samples in like that. (Showing specimen.)

Mr. Jackson: If I made my samples of the same size as that piece of opaque glass you have in your hand, and, as I am making plates today, I should take a sample of the product of the pottery as we are making it, and make the sample the same size and then standardize it, I would then have a standard value, wouldn't I, that would fix my value for the present production?

Mr. Priest: Yes, sir.

Mr. Jackson: Now then, suppose, for instance, I should in a month hence wish to use different clay, different flint or different feldspar, by observing the same size all the way through, I could get a relative value of the translucency?

Mr. Priest: Yes.

Mr. Jackson: Comparing it with my standard?

Mr. Priest: Yes.

Mr. Jackson: Now that is the point I want to get at. What we want is a relative value on our own factory?

Mr. Priest: Yes.

Mr. Jackson: In selling our products, we are not going to tell this man and that man that we have a translucency of any given value; he will decide that for himself, but what we want is to fix a value for ourselves, some standard in our own factory.

Mr. Priest: You could, for instance, make up a series of five, ten or a dozen plates of varying translucency.

Mr. Jackson: It does not necessarily have to be a plate.

Mr. Priest: And you could have these measured on the instrument and preserved in your office as your working standard. You would probably, for your purposes, have an instrument to measure them from time to time, and you could perhaps tell well enough for ordinary commercial purposes by merely comparing one with the other.

Mr. Jackson: In making that original standard, we will assume that I use one-eighth inch thickness; now if that is my standard in succeeding work, I will have to adopt that as my standard in thickness all the way through or will my values change thereby?

Mr. Priest: You can make measurements for thickness. By making the proper computations, corrections for reflection at the surfaces, etc., you can obtain what you might call the translucency per unit thickness. You don't need to measure with unit thickness, you can measure with some other thickness. Say you take a sample 3 millimeters thick and get a certain value for that; from that value you can compute what it should be for one millimeter. To avoid computation, it would be convenient to make all your samples of unit thickness, but it would not be necessary.

Mr. Jackson: But it would be desirable?

Mr. Priest: It would avoid the arithmetic and algebra afterwards.

Mr. Jackson: Even that would not be as satisfactory as to have it purely relative as you lay them right down before you.

Mr. Priest: I don't know enough about manufacturing methods to know how nearly you can reproduce them.

Mr. Jackson: It is very difficult to get exactly the same.

Mr. Priest: You could grind them all of the same thickness though?

Mr. Jackson: You don't think that would interfere with it?

Mr. Priest: Well, it would grind the glaze off.

Mr. Jackson: It would affect the translucency a whole lot, wouldn't it?

Mr. Priest: It would not affect much the unglazed ware, if they were unglazed in the beginning. They ought to be ground, however, and polished to a standard condition of surface.

Mr. Purdy: That's the point, they'd have to be polished, if you ground with glass.

Mr. Priest: What you lost by reflecting would depend on the condition of the surface.

Mr. Purdy: Mr. Jackson wants a system by which he can measure trial pieces that vary silghtly as a pottery body will in manufacturing. Prof. Bleininger has tried to sound the death knell of the old wedge we used to use for the measuring of translucency. In that test, we slid it past a slot, behind which was a lamp of a certain power, and marked the point on the wedge where the light just disappeared, then using the thickness of the wedge at that point as a numerical expression of the translucency. The method is subject to inaccuracy. This we have granted, and if the observer is tired or fresh, it affects the result. We also recognized that the measurement was not the real measure of translucency, but it surely was a relative measurement such as Mr. Jackson and Mr. Stover have been talking about. How large a value is that which you have expressed in your formula?

Mr. Priest: I don't quite get what you mean.

Mr. Purdy: How large a factor is that difference of thickness?

Mr. Priest: It all depends on what a is, that is, how much is transmitted by the unit of thickness.

Mr. Purdy: I think we are talking at cross purposes; we know that a thick piece is not as translucent as a thin piece.

Mr. Priest: Certainty; say that a millimeter transmits 50 percent then two millimeters will transmit 50 percent of 50 percent, and three millimeters will transmit 50 percent of 50 percent of 50 percent. It is a geometrical ratio instead of an arithmetrical ratio.

Mr. Purdy: We made changes in composition and got different translucencies and explained these differences in terms of thickness through which a given light would cease to penetrate. In these studies as in pottery ware, translucency is not altogether dependent on thickness. When comparing effects of different materials or different compositions, a measure, such as I described and wanted by Mr. Jackson, will give results.

Mr. Priest: Well, that's all right.

Mr. Bleininger: I still do not agree with Mr. Purdy. I think the relation is not a linear one. If it is not right, why not look for something better? In spite of what has been said, it is evident that in the methods previously used, the question of the thickness entered into every determination.

Mr. Purdy: Mr. Priest said it was all right.

Mr. Priest: I said it was all right for an empirical method; I think that which Prof. Bleininger takes exception to is not having something of more fundamental significance.

Mr. Purdy: To this I agree. I know the relation is not a linear one. But does it matter whether it is arithmetical or geometrical when the figures are small?

Prof. Orton: If I understand Mr. Priest correctly, he said it would be possible by means of this method, to standardize a series of discs made by the potter so that the potter himself could, by subsequent comparisons, get close enough to the relative translucency to determine where a given plate fell between any two members in the series.

Mr. Priest: I believe that is all that would be required for commercial purposes.

Prof. Orton: Would it be possible to make anything but very crude comparisons when depending upon the untrained eye of the commercial observer?

Mr. Priest: It would be very crude unless you had some apparatus for observing by which you could bring them together in a photometric field. To get the maximum accuracy, you must bring the two fields you want to compare immediately together, so that when they are matched, the line between them disappears, and that is the criterion of them being alike.

Prof. Orton: It would not be possible then, by previous grading of the little discs to hold the relative light intensity in the eye long enough to make a correct comparison?

Mr. Priest: No.

Prof. Orton: The images of the two materials to be compared in your instrument are not superimposed, but are merely brought side by side for a close comparison, as I understand?

Mr. Priest: Yes, and when they are alike, you won't see the line, you will only see the one field.

Prof. Orton: Then in your opinion you must have some form of photometric apparatus to make a comparison of the intensity of the transmitted light for the two pieces of ware?

Mr. Priest: If you want to get accurate values.

Prof. Orton: Could you arrive at any decent kind of precision without it?

Mr. Priest: Well decent is not a quantitative word; perhaps you could get 10 percent, at a guess.

Prof. Orton: Do you think you can get enough closer by your method than the crude comparison by which a potter puts his finger behind a plate and observes its shadow and then puts up another and decides which is the more translucent of the two?

Mr. Priest: Well, in regard to both of these methods, I think the method of watching for the disappearance of a light is a very bad method. Two brightnesses can be adjusted to equality with reliability and precision, but when you slide a wedge along in front of your eye until a light disappears, as the chemist would say, you haven't any end point, your end point is no good.

Mr. Purdy: Would not this method that Prof. Orton has been describing be as accurate as the colorimetric method? There, it is a question of intensity of light through a solution.

Mr. Priest: In the chemical colorimeters, the ones made according to the best design bring the two fields together.

Prof. Orton: Could a cheap form of photometric apparatus be made to compare for translucency, discs of pottery, for just such purposes as Mr. Jackson has in view?

Mr. Priest: Yes, such an apparatus could be made for 10 dollars, I suppose.

Mr. Priest: I have not yet got all the information I want and I would like to inquire just what your purpose is in wanting to measure translucency? Why are you interested in it, what ends does it serve, and what precision and what accuracy is desirable? Then, knowing those things, I could more intelligently advise you as to how to reach the desired results.

Mr. Stover: I think I can answer that, at least from the standpoint of a good many potters. It is purely a commercial point. When you put either a fine grade of china or a bone china product on the market, you come into competition with German, French and English products. To compare the translucency you hold each plate to the light and compare the distinctness of the outline of the figures of your hand when introduced on the opposite side of the plate, between the plate and the light. With the American plate, you can hardly tell whether you are holding one or three fingers up, but with the foreign plate, you can see the least little movement of the finger back of the plate. After such a comparison, your American china is ruled off the market.

Mr. Priest: It is a question of aesthetics then?

Mr. Stover: It is a question whether or not you can produce a certain degree of purity.

Mr. Mayer: This question is important for the potter; a piece of ware depends on its translucency for the value it has on the market, and we want to see how closely we can get to the high grades of English, French and German china, on account of their value; it is a commercial proposition from beginning to end. We have no accurate measurements now that we can apply, absolutely none, and we have learned a great deal this afternoon. Here is an apparatus that will do it, there is no question about that. To get at the thing, it will be necessary to get the apparatus ourselves or to send the discs to some one who will give us the relative translucency as compared to some standard that we will have to provide.

Prof. Parmelee: I would like to ask Mr. Priest whether he would be willing to furnish, for the Transactions, a sketch of the apparatus that he said would cost about 10 dollars, and would be sufficiently serviceable?

Mr. Priest: For merely comparing two specimens?

Prof. Parmelee: Yes, comparing two saucers or two plates.

Mr. Priest: Yes.

AN UNUSUAL CASE OF PINHOLING OF GLAZES

BY H. J. KNOLLMAN

The pinholing of glazes is a problem that is encountered to a more or less extent by practically anyone requiring the use of the various types of common glazes. The pinholes themselves are of different types, depending upon the kind of glaze considered. The type of pinhole, here referred to, is that occurring in glazes that are more like glasses, and not to such types of glaze where the pinhole is due to failure of drying or shrinkage cracks in completely heating up.

This phenomenon may appear in various stages of development. One rather common stage, especially where the glaze is heavy enough, is where it contains numerous small bubbles under the surface of the glaze. When these bubbles come to the surface and leave small depressions, they are designated as pinholes. If the trouble becomes an exaggerated one, it may take on the form of blisters. On the other hand, if it is only slight, we have the production of an eggshelled surface. In the decorating kiln, a defect similar to and allied with pinholing is known as spit-out.

In Seger's *Collected Writings,* we find that he recognized these defects and attributed them to be due to sulphuring, the sulphates being either introduced on purpose, or through impurities in glaze ingredients, water used in the preparation of glaze or by kiln gases. Too early interruption of the glost fire or too hard boiling of the glaze are also given as causes.

In Volume II, *Transactions American Ceramic Society,* Mr. S. G. Burt attributed the bubbling and blistering of glazes to sulphates present as a scum on the body, rather than sulphuring of the glazes themselves. The solvent action of the glaze resulted in the decomposition of the surface sulphates and the freeing of gas. He got around the trouble by using a higher silicate glaze, on the theory that it would have less solvent action on the body. A change of body also helped the trouble. Mr. E. Mayer, on the other hand, found that softening the glaze generally helped the trouble.

Mr. Gray, in Volume VII, *Transactions American Ceramic Society,* found that too quick cooling of the glaze caught it in a boiling condition without giving it time to smooth out, which resulted in bubbled or blistered glazes.

In Volume IX of the *Transactions,* Mr. R. C. Purdy, in his article on fritted glazes, attributed the pinholing of glazes to carbon which had been entrapped by the glaze during the fritting stage of glaze formation. This carbon would later go out through the glaze as the gas, carbon dioxide, leaving pinholes in the glaze.

It is the purpose of this article to set forth some observations and theories which tend to show that the pinholing of glazes is primarily due to the viscosity of glazes, and that under certain rather unusual conditions, it is essentially a water smoking phenomenon. The type of glazes particularly referred to are the medium fired cone 8 to 10 porcelain glazes, such as are used on green vitreous and fireclay sanitary ware. They are burned in commercial muffle kilns, soft coal being the fuel used.

Pinholes would appear in the glaze in varying numbers and often in a somewhat elusive and mysterious manner. It was a rather common experience to have several kilns with the ware coming out badly pinholed, then presently a kiln would come along in which the ware was altogether free from pinholes. The good glaze was not confined to any particular kiln or kilns. Yet, from a study of the method of firing and kiln records, no difference in the details of firing could be detected, and no satisfactory reason as to variation in firing producing the pinholes could be advanced. Even in the same kiln, at times, part of the ware would be badly pinholed, while part would be comparatively free from them. At times, a piece here and there would be entirely free from pinholes, while the rest of the ware would contain many of them. Hence the pinholes often appeared in a sort of hit or miss fashion, although as a rule they appeared with great regularity.

Carbonization and sulphuring of glazes have been the two main theories that have been advanced as to the cause of pinholes. To see which of these, or if both, were the cause of the

trouble, many variations in firing were tried, but without any tangible results. It did not seem to make any material difference whether the burns were reducing or oxidizing during the different stages of the burn. The analysis of the waste gases under normal firing conditions showed the burn to be oxidizing throughout. Even after fresh fuel had been put on the fire, it required but a few minutes for the burn to become an oxidizing one. Since the pinholes might be present in such numbers as to dim the lustre of the glaze, the trouble could hardly have been due to carbon. Moreover, it is hard to see how carbon could have been entrapped in the interior curved surface of a piece of ware, which was not incapable of being pinholed as badly as the rest. As the ware was carefully brushed free from all dust before glazing, the trouble was not due to any such conditions. Thus it seemed as though the trouble must be due to sulphuring in some form or other.

During one of these worst sieges, it was found that the amount of clay ware present in the kiln had a considerable influence on the apearance and degree of pinholing. Kilns containing large massive pieces of fireclay sanitary ware with little or none of the smaller vitreous white ware would almost invariably bring out ware in which the glaze was free from pinholes. If, however, the amount of fireclay and green vitreous ware approached half and half, pinholes would be almost sure to be present, while if the kiln was completely filled with small vitreous ware, the ware would always be badly pinholed. If the kiln contained a large amount of fireclay ware, such as bath tubs, etc., it could not be filled as solidly as in the setting of all smaller ware, and as a result there was a large open space in the top of such a kiln, whereas the other kilns would be filled more solidly and were set so as to be filled nearly to the crown of the muffle.

This condition led to the conclusion that the water smoking must have considerable to do with the trouble. The moisture coming off from the green ware during this early stage of firing would combine with the SO_2 and SO_3 from the fuel gases to form sulphuric acid, which would then be deposited upon the ware as an acid dew and would soak into the glaze and ware to a more or

less extent, depending upon the length of time to which the ware would be subjected to these moist gases. The large fireclay goods are necessarily heavily grogged and so are more open and porous, which favors the rapid and free expulsion of the water. This water vapor would naturally go to the top of the kiln, where it would stay until expelled entirely by the action of increasing heat. Since the top of the kiln does not contain any ware in this case, the heat can get at the ware as a whole more rapidly and so help to expel the water from the clay more rapidly. Hence this ware escaped being sulphured to any extent, since the moist sulphurous gases were not allowed to find lodgment on the ware.

If, however, more of the green vitreous ware is placed in with the fireclay, the kiln is not only set denser, but more water is also introduced, due to the mechanical and chemical water present in the clay. Hence, in kilns which are completely filled with all green vitreous ware, especially when filled to capacity, we have the conditions most favorable to sulphuring. The vitreous ware is a dense body, and when it is set close together in a kiln, it is obvious that it will take a much longer time for the heat to expel all the moisture. Consequently not only much more moisture and sulphuric acid is formed, but the ware is subjected to this sulphuring to a greater extent as the moisture deposits on the ware from point to point until finally driven entirely off. This seems to be the most tenable theory as to why the kilns filled with all vitreous ware should be pinholed so badly, while those set more openly would contain ware free from pinholes, other conditions remaining constant. It seems to be due to a sort of mass action effect, in which the time factor plays a part.

Quite often there are a few pieces present in a kiln that are comparatively free from pinholes, a few more pieces that have only a few pinholes, while the rest are heavily pinholed; these facts indicate that it is a dew point phenomenon. A spot, which seemed to be particularly favored, is that immediately around the center well hole of the kiln. Now this spot naturally becomes hot more rapidly than the other parts of the kiln, and this heat is conveyed to the ware at this point. The ware is thus heated up sooner, the moisture expelled earlier, and the piece soon

reaches a temperature beyond the dew point, and as a result the wet sulphurous gases do not deposit on the ware at this point, but deposit on, and are absorbed by the colder pieces nearby. This point most readily explains the peculiar selective and somewhat mysterious appearance of pinholes in the same kiln. All kilns, no matter how carefully constructed and fired, have hot and cold spots, and there are numerous counter currents set up within the kiln, some being hotter than others. So, the ware that is heated up the soonest and subjected earlier to the hotter currents will not take up as much moisture during the water smoking period, as that which stays cold the longest, and as a result such ware will not be pinholed so badly. The ware which happens to be located in a warm spot will thus be favored over the rest. The colder ware will not only catch the moisture from the hotter ware, but it will require a longer time to expel the moisture from such ware. The more uniform the heating up of the kiln during this early stage, the more uniformly will the ware be pinholed, if it is subject to this trouble. The ware in front of the kiln doors is generally pinholed worst, no doubt due to the fact that this is generally a cold spot, and that more moisture is likely to be present at this point because of the freshly mortared doors.

The appearance of pinholes here and there in a kiln may be explained by still another illustration. In a kiln, filled with all small vitreous ware, the smaller pieces were often not as heavily pinholed as the larger ones. Thus a glaze, on a small 4 in. by 4 in. trial, would quite often come out entirely free from pinholes, while the same glaze applied to the commercial piece and placed alongside the small trial in the same kiln, would come out full of these little pinholes. In fact, quite a few glazes would behave in this manner. When applied to small trials, they would come out satisfactorily, but when they were applied to the commercial ware and burned under the same conditions, they would be heavily pinholed. This fact strongly indicates that the trials, being small and capable of heating up quickly, were not sulphured as heavily during the water expulsion period as the commercial ware.

In order to eliminate the pinholes present in the glaze from

the first fire, it was the common practice to refire such ware, whereupon it would then come out of the kiln good. Now if a small amount of the green ware, about one percent for example, was placed in a kiln containing otherwise all ware to be refired, this green ware would also come out free from pinholes. The length of burn and manner of firing was the same as when a kiln containing green ware was fired. This refired ware, of course, had lost all its water, so the only moisture present was that coming from the small amount of green ware, the wadding used in the setting of the ware and whatever moisture was present in the fuel. Since the amount of moisture in this case is small, the result was that the water smoke was ineffective, and so the green ware that was present escaped being sulphured heavily enough to be pinholed to any extent. If only a few pieces of green ware were present among all refired, the green ware could be depended upon to come free from pinholes.

In order to overcome this trouble, under the worst conditions as well as the best, it was found necessary to soften the glaze considerably. Whether present as the free acid or as sulphates in the glaze, these once more break up into the SO_2 or SO_3 gases under the influence of the various reactions during the increased heat treatment and the fusing of the glaze. If the glaze is too viscous and stiff, it will not only let out these gases with great difficulty, but after they have escaped, the glaze will remain rigid and a pinhole will be the result. If, however, the glaze is more fluid and has a lower viscosity, it not only lets out these gases more readily and easily, but it is also capable of flowing sufficiently to heal up the depressions made by the escape of the sulphurous gases. In this way a smooth uniform surface will be produced instead of a surface pitted all over with pinholes.

The composition of the glaze is consequently of considerable importance in the elimination of pinholes. In a series of trials covering the porcelain glaze field, it was found that as the viscosity of the glazes was increased, the trials would be pinholed in proportion. A softer R O content, keeping the Al_2O_3 and SiO_2 content constant, would give glazes having less pinholes than a harder R O content. On the other hand, keeping the R O con-

stant, an increase of Al_2O_3 would in general lead from scummed to bright glazes free from pinholes to glazes having an increasing number of pinholes, until they would go into the dull or mat field. The same was true of increasing amounts of SiO_2 to even a greater extent. A slight increase, at times, was sufficient to throw a good glaze over to a pinholed one, although the change was not sufficient to affect the maturity to any noticeable extent. The use of good fluxes is a very material help, and the composition of glazes of this type free from pinholes is narrow, under the rather unusual conditions described.

The fact, that the pinholed ware on being refired comes out of the kiln free from pinholes, also shows the influence of viscosity. We know that it takes a certain amount of heat work to accomplish the fritting and fusing together of the various constituents in a glaze, and that after this is accomplished, additional heat will increase the fusibility and fluidity of the glaze. Hence if the glaze is refired, it is not only very much more homogeneous than it was the first time, but the heat work, that would be required to cause the fluxing reactions to take place, is used instead to increase the fluidity of the glaze, and consequently sufficient flow is obtained to completely heal over these defects. The fact that the range of fritted glazes is considerably broader with regard to this defect is due to this reason.

Application of a heavy coat of glaze on the surface of the ware aggravates this trouble. The trouble can be avoided in many instances by applying a thin coat of glaze, but the glaze is then very apt to have an eggshelled appearance, or else will not have sufficient gloss to give a satisfactory surface for sanitary ware. Where high gloss is required, a very thin coat of glaze will not do. A thick layer of glaze will offer more resistance to the escape of the gases and will not be so apt to heal up the passages thus made, as a thinner layer.

Faster firing will also be of decided benefit in some instances. Faster firing during the early stages of the burn will cause the water smoking period to be of shorter duration, thus lessening the sulphuring period. A sharp quick fire at the finish of the burn also results in increased fluidity of the glaze and lessens

the volatilization of the volatile constituents. Where we have a glaze that has a slight tendency to pinhole, faster firing is an effective way of remedying the trouble, provided the ware will stand such treatment.

While there is undoubtedly more than one cause of the pinholing of glazes, the sulphuring during the water smoking period certainly seems to be the main one; since it is possible to use a harder, more viscous glaze when the water smoking is reduced, while a softer and more fluid glaze is necessary when the amount of moisture is large. The point to be emphasized is that the appearance of pinholes it due to too great viscosity of the glaze. There may be certain conditions where the production of non-pinholing glazes, especially raw glazes, becomes a difficult problem.

ANTIMONY COMPOUNDS AS OPACIFIERS IN ENAMELS

BY HOMER F. STALEY

That compounds of antimony could be used with some success as opacifying agents in enamels has been known for a very long time. However, only during the last ten or fifteen years have they been employed on a large scale in commercial operations. The many difficulties involved in the use of antimony compounds are the obvious reasons for their failure to come into general favor earlier. The constantly rising price of tin oxide and the growth in the technical ability of enamel makers are the causes for their more general employment during the last few years.

The first experience of the writer with antimony compounds as opacifiers was in 1906, when he attempted to use domestic oxide of antimony in an enamel for cast iron, in an enameled-iron sanitary ware plant of which he was then superintendent. This first attempt was not successful. We were able to control the glass and working properties of our enamel, but the color of different batches varied through various light tints of yellow, green and blue in what was then an inexplicable manner. Although the use of the material on a commercial scale had to be abandoned at that time, my own interest was aroused, and during the intervening years I have dealt with compounds of antimony as opacifiers both in extensive laboratory experiments and on a commercial scale in the plants of half a dozen different enameling companies. My reason for making this statement is that I do not wish any one to draw the inference that the statements made in this paper have a definite relation to the shop practice of any of the firms with which, the writer has been connected, either as a full-time employee or in a consulting capacity.

At this point, I might say that the same general principles have been found to apply to the use of all the compounds of antimony with which I have had experience. Since antimony tri-

oxide has been somewhat cheaper than sodium metantimonate and other antimony bearing opacifiers, and could be made to give as satisfactory results, my efforts have been toward the best utilization of the oxide. R. E. Brown[1] has described experiments with oxide of antimony in enamels for cast iron. The enamels I have used have been of a rather different type from those given by Brown, being considerably more fusible.

Antimony compounds can be used as opacifiers in enamels both for sheet steel and cast iron. Since the enamels in common use for sheet steel contain little or no lead, are comparatively high in boric acid, and are more refractory, *i. e.*, higher in feldspar and silica, than enamels for cast iron, the difficulty in adapting sheet-steel enamels to the use of oxide of antimony, or other antimony compounds, is much smaller than in the case of the types of enamels in common use on cast iron. Since the latter present a similar but a more intricate problem, a discussion of the methods to be employed in adapting them to the use of antimony will be the more profitable.

The technique of antimony enamels, in as far as it differs from that of tin bearing enamels, naturally falls under three heads: control of gloss; control of color; and elimination of dark specks. The discussion will follow this outline.

CONTROL OF GLOSS

Enamels for cast iron are glasses which, compared to ordinary glasses and glazes at the same temperatures, are quite fluid and tend to crystallize readily. This crystallization produces a lusterless or mat surface.

Viscosity. The simplest method of overcoming the tendency to crystallize is to make the enamel more viscous at the temperatures at which crystallization takes place, thus reducing the ease with which crystals can form. Silica alone melts to a very viscous glass; and, in general, addition of silica to any melt produces a more viscous glass. Silicates high in silica also melt to viscous glasses. If silica (flint, sand) or feldspar (a high silica compound) is added to an enamel, the enamel is rendered more viscous at all temperatures and the tendency to become dull from

[1] *Trans. Amer. Cer. Soc.*, Vol. XIV, p. 740.

crystallization is lessened. Since the working temperature of the enamel is raised by this procedure, the method is of little value in controlling the gloss of enamels that must mature at temperatures rather rigidly fixed by shop practice and conditions.

Boric oxide alone forms a very viscous glass at low temperatures, but, as shown by the writer,[2] the viscosity of the glass decreases rapidly as the temperature increases. The glass was found to be three times as viscous at 700°C. as it was at 1000°C. The first temperature approximates that at which crystallization takes place in enamels, and the second is near the maturing temperature of most enamels for cast iron. The borate glasses of any given base resemble silicate glasses in behavior and become more viscous as the percentage of boric oxide increases. The viscosity of borate glasses decreases with rise of temperature in the same general way as that of boric oxide glass, but not as rapidly. The effect of increasing the boric oxide in cast iron enamels is to increase the viscosity of the enamels at temperatures at which crystallization is liable to take place and thus to decrease the tendency to matness without raising the maturing temperature of the enamel. In fact, the maturing temperature is lowered in the case of many enamels.

Concentration. With the exception of boric oxide, all these materials in enamel compositions known as fluxes, namely, the oxides of lead, zinc, sodium, potassium, calcium, barium, magnesium and the various fluorides, tend to form compounds which are easily crystallizable. Lead oxide differs from the others in that its compounds do not crystallize until a very low temperature is reached. Since the enamel composition will be too viscous at low temperatures to allow crystallization to take place, lead compounds do not crystallize from enamel compositions. Of course the tendency for any compound to separate in the crystalline form from a cooling glass is decreased by decreasing the amount of the compound in the glass. Therefore, the amount of each of the fluxes except boric oxide and lead oxide should be kept low. This means that as the total amount of these crystal forming fluxes increases, a greater variety must be used.

[2] The Viscosity of Molten Glasses. *Original Communications, Eighth International Congress of Applied Chemistry*, Vol. V, p. 127.

Sulphur. It is well known that sulphur compounds in an enamel tend to separate on the surface causing a diminution of luster. Antimony enamels are no more subject to this defect than other enamels; but, owing to the fact that the luster of antimony enamels tends to be impaired by other causes, especial care should be taken to see that all materials are as free from sulphur as possible, and that slight opportunity is given for the enamel to absorb sulphur compounds during smelting or application to the ware.

Enameling Technique. Any necessity for prolonging the enameling operation that involves partial cooling and reheating of the enamel after the enamel coat is matured furnishes favorable opportunity for the development of crystallization and dull finish. Owing to their composition, antimony enamels are especially liable to crystallize. Therefore, considerable care must be taken to avoid the necessity for patching by having all castings in the best of shape for enameling before the operation commences and by employing the most skillful workmen available to apply the enamel.

Type Formulae. The High Boric Oxide, No Lead Type. As is well known, an enamel containing twenty to twenty-five percent of lead oxide, as is the case in ordinary tin bearing enamels for cast iron, gives a lemon-yellow color when oxide of antimony is used as the opacifying agent. The most simple type of antimony enamel is derived from leadless tin-bearing enamels closely related to those used for sheet steel. Being free from lead and comparatively high in one or two crystal forming fluxes, these enamels must necessarily contain a large percentage of boric oxide if they are to have a good luster.

Enamel No. 1 in Table I shows the composition of such an enamel taken from a publication[3] by Mr. George P. Fisher and the writer. This enamel as it stands could be converted into an oxide of antimony enamel by simply replacing the tin oxide by antimony oxide. In this country, however, it is cheaper to buy boric oxide in the shape of borax than as boric acid, and the tendency would be to use no boric acid but a large

[3] Leadless Enamels by Homer F. Staley and George P. Fisher, *Trans. Amer. Cer. Soc.*, Vol. XV, p. 626.

TABLE I—RAW WEIGHTS

	No. 1	No. 2	No. 3	No. 4	No. 5
Feldspar	410	425	422	425	425
Boric Acid	222	...	...	...	...
Borax	245	500	151	325	200
Soda Ash	...	...	81	57	57
Sodium nitrate	27	27	27	27	27
Barium carbonate	...	...	90	90	90
Whiting	...	...	27	27	27
Fluorspar	...	...	122.5	100	85
Cryolite	120	100	...	...	...
Zinc oxide	125	125	150	100	80
Red lead	...	...	...	...	102
Antimony oxide	...	75	...	75	75
Tin oxide	80	...	83	...	...

CALCULATED MELTED WEIGHTS

	No. 1	No. 2	No. 3	No. 4	No. 5
Feldspar, K_2O, Al_2O_3, 6 SiO_2	410	425	422	425	425
Boric acid, B_2O_3	125	...	...	...	...
Borax B_2O_3	90	185	56	120	75
Borax Na_2O	40	80	24	52	32
Soda ash, Na_2O	...	...	47	33	33
Sodium nitrate, Na_2O	10	10	10	10	10
Barium carbonate, BaO	...	...	70	70	70
Whiting, CaO	...	...	15	15	15
Fluorspar, CaF_2	...	...	122.5	100	85
Cryolite, Na_3AlF_6	120	100	...	...	...
Zinc oxide, ZnO	125	125	150	100	80
Red lead, PbO	...	...	...	...	100
Antimony oxide, Sb_2O_3	...	75	...	75	75
Tin oxide, SnO_2	80	...	83	...	...
Total	1000	1000	1000	1000	1000

amount of borax. This change, with a few incidental rearrangements of proportions, would give us enamel No. 2 as an example of the high boric oxide, no lead, type of antimony enamels.

The Medium Boric Oxide, No Lead Type. Enamels as high in boric oxide as those just discussed are not in general use among cast iron enamelers in this country. When attempting to change from tin bearing enamels to antimony bearing, the natural procedure for American manufacturers was to start with a formula similar to those they had been using, to reduce or eliminate lead oxide, and make such other changes in composition as were found necessary. The formulas of the enamels in common use for cast iron are quite complex, and consequently the antimony bearing enamels derived from these are complex.

Enamel No. 3 shows a leadless enamel derived, in a manner described in the article by Fisher and the writer already quoted, from a formula typical of the lead bearing enamels in use in this country. Although this enamel had a beautiful gloss when tin oxide was used as the opacifying agent, the gloss was not satisfactory when oxide of antimony was substituted for the oxide of tin. Following the principals discussed above, the fluorspar and zinc oxide were reduced in amount, and the borax was increased. This gave enamel No. 4 containing twelve percent of boric oxide and not over ten percent of any other fluxing oxide. The finish of this enamel was very good. Enamel No. 4 may be taken as representative of a type of antimony enamels containing no lead, a medium amount of boric acid, and a diversity of other fluxing ingredients no one of which is present in large amount.

The Low Boric Oxide, Lead Bearing Type. Leadless enamels are not satisfactory in working properties. They craze and chip with seemingly no provocation, do not stand patching well, and they are not as opaque as enamels with the same amount of opacifier but containing lead. This latter defect is probably due to the fact that lead bearing enamels are heavier than leadless ones, and therefore the opacifier is less diffused in the lead bearing enamels. For these reasons, many enamelers prefer to use as much lead in their antimony enamels as is consistent with a satisfactory color. As the lead is increased, the boric oxide can

be decreased. At the same time the other fluxing oxides present in largest amounts will be reduced somewhat. Enamel No. 5 derived from enamel No. 4, is an example of the low boric oxide, lead bearing type of antimony enamels. It will be noted that this enamel is the most diverse in composition of the three types of antimony enamels, since it contains one more fluxing oxide and, with the exception of lead oxide, not over eight and a half percent of any one.

CONTROL OF COLOR

One of the great difficulties in the use of antimony compounds in enamels is the wide variations in color, or rather tint, encountered. These vary from light tan or yellow through cream, a fair white, light green, and light blue to a decided robin-egg blue. The hue and tint obtained depends on the composition of the enamel, and the heat treatment given it during melting.

Effect of Composition. Lead Oxide. It is well known that antimony enamels containing large amounts of lead give a yellow color. For instance, a beautiful lemon-colored enamel was obtained simply by substituting oxide of antimony for oxide of tin in Enamel E 4, shown on page 624 of the article on leadless enamels by Fisher and the writer. Entire elimination of lead oxide from antimony enamels is not desirable, however, for reasons stated above; and by experiment it has been found that enamels of fair color can be made containing considerable amounts of lead oxide. In amounts up to ten percent, lead oxide tends to impart a very faint yellow cast to the enamels. The tint is persistent, not altering with heat treatment. This color may be so combined with some other color, generally blue, that they are both practically neutralized, or the proportions of the two colorants may be such that a light green color is produced.

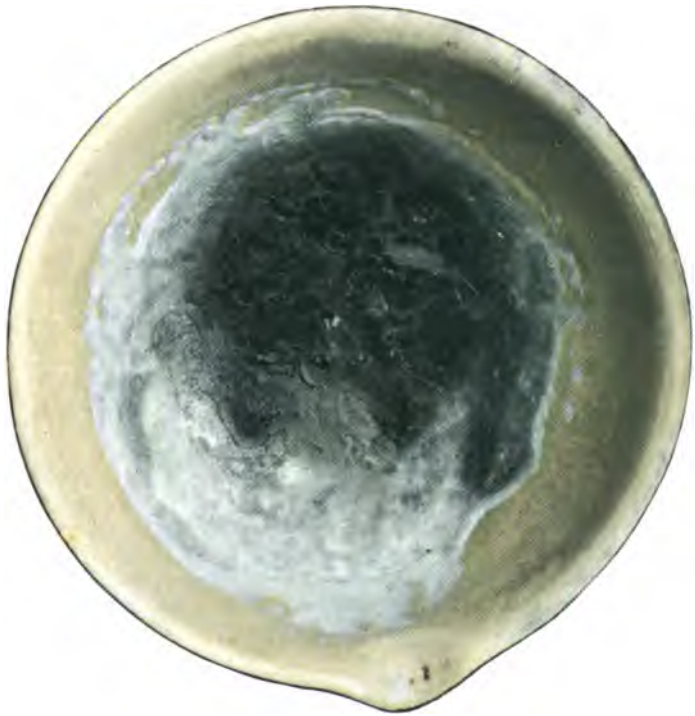
Boric Oxide. If commercial antimony oxide and boric acid are melted together, a translucent brown glass is produced. The source of the color is unknown, is may be due to impurities. If this glass is used as a component of an enamel, an opaque white enamel is produced. All antimony enamels are a decided tan during the first stages of the smelting process. and the depth of

this color increases as the boric oxide increases. This tan color of the enamels is thought to be due to the same causes that produce the brown color in antimony oxide—boric acid mixtures. As the smelting continues this color gradually fades. However, if the amount of boric oxide is large, and no other neutralizing color is present, the enamel may not become a good white unless the smelting is continued for a long time at high temperatures. In such cases the opacity of the enamel is reduced due to the gradual solution of the opacifying agent. For this reason, it is desirable to introduce some ingredient that will form a color to neutralize the last traces of tan or yellow. Cobalt oxide is sometimes used for this purpose, but generally the neutralization is accomplished, consciously or unwittingly, by the introduction of some form of calcium as explained below.

Calcium Compounds. During the winter of 1912-1913, the writer with the aid of Mr. Samuel Rusoff, made a rather extended study of the effect of variation in composition of antimony enamels on the tints produced. Very much to our surprise, we definitely established the fact that calcium, introduced either as the carbonate or fluoride, had a decided effect on the hue of the enamel, always tending to produce blue tints. We were unable to explain the production of these tints, but they seemed to be peculiar to antimony enamels, since they do not occur when tin oxide is used as opacifier. The intensity of the color increases with concentration of calcium compounds and with duration of heat treatment.

Since the development of this blue color is a serious drawback to the use of oxide of antimony enamels for high grade ware, we have spent considerable time in trying to determine its origin. I shall not attempt to give a detailed account of the several hundred experiments made in this search, but shall give a simple summary of the work.

In order to render the problem as simple as possible, we started with as simple a formula as could be devised from the ingredients commonly used in this country. The enamel contained the following ingredients: feldspar, boric acid, antimony oxide, and a little sodium nitrate. No blue color was produced in this



enamel. We replaced part of the boric acid in this base mixture with various fluxing materials used ordinarily in making white enamels, using one at a time. The materials used were: soda ash, borax, barium carbonate, barium fluoride, calcium carbonate, magnesium carbonate, fluorspar, cryolite, zinc oxide and lead oxide. Only one of these mixtures, the one containing fluorspar, gave the blue color. This was of a decided blue tint. Evidently fluorine had something to do with producing the color.

In the next series cryolite was made a constant constituent of the base mix. The only new element introduced by this addition was of course fluorine. To the base melt as thus altered, additions, one to a melt, were made of the following: soda ash, borax, barium carbonate, calcium carbonate, magnesium carbonate, zinc oxide and lead oxide. The only one of these mixtures giving a blue color was the one containing calcium carbonate. It is obvious that calcium and fluorine together had an influence on the color, since mixtures containing either of these ingredients without the other did not give the blue color.

From this point I proceeded to systematic blends of more complex nature, producing formulas such as are in ordinary use in plants. Of all these mixtures, only those containing both fluorine and calcium gave blue colors. In working with a large variety of antimony oxide enamels in enameling plants, I have always found that increase of calcium increased the tendency of the enamels to come blue, and decrease of calcium decreased this tendency.

The next step was to attempt to isolate the coloring principal in the simplest mixture containing it. This mixture, it will be remembered, consisted of feldspar, boric acid, antimony oxide, sodium nitrate, and fluorspar. By eliminating these ingredients one at a time, I found that feldspar and sodium nitrate were not essential to the production of the color. Owing to greater concentration of the coloring principal, the color was much more pronounced. The materials in the mixture were thus reduced to four: antimony oxide, boric oxide, calcium, and fluorine. Although I made a large number of attempts with all sorts of combinations, I was not able to produce any shade of green or

blue, if I eliminated any one of these materials, or replaced any one of them by any of the other materials commonly used in making white enamels.

Since the color was not developed by any combination of three of these materials, it was fairly certain that it was not due to impurity in any one of them. However, in order to be absolutely sure, I made up mixtures from carefully analyzed materials. The only coloring oxide in the mixture as compounded was a 0.002 percent of ferric oxide. These mixtures gave a deep blue color. When the melts were tested for metals, none were found except antimony.

When working with commercial materials the effect of the temperature at which these colored melts were drawn was as follows: 900°C. tan, 1000°C. greenish yellow, 1050°C. dark green, 1100°C. greenish blue. These mixtures were fired at the rate of 100°C. an hour. With a slower rate of heating the color changes took place at lower temperatures. With very rapid heating, the whole melt instead of being a uniform color at the end of the heat, would consist of a layer of green or blue opaque slag covering a layer of white enamel. The condition of the kiln gases as long as they were kept oxidizing, or at least nearly neutral, seemed to have little effect on the color. Of course strongly reducing conditions cannot be used in making white enamels. When nearly pure materials were used the differences in the color reactions were that at low temperatures the melts were a light cream instead of tan, and at high temperatures the greenish tint in the blue was much less marked. The commercial oxide of antimony contained one percent of sulphur and the nearly pure oxide only 0.001 percent. The yellow color in oxide of antimony enamels at low temperatures, which gradually fades as the temperature rises is probably due to sulphur. Of course yellow mixed with blue gives green at intermediate temperatures.

While we feel safe in saying that the blue coloring matter in these glasses contains antimony oxide, boric oxide, calcium and fluorine, we do not know the constitution of the coloring matter. Probably a very small amount of our melts went to make the coloring material. This is shown by the fact that as long as the

four materials were present, the proportions of the various materials had slight effect on the color. Probably the deepest color was obtained from the following mixture:

Antimony oxide	1
Boric acid (hydrated)	2
Fluorspar	1

EMPIRICAL FORMULA

$1.0\ Sb_2O_3,\ 3.7\ CaF_2,\ 4.65\ B_2O_3$

A reproduction of the color produced by this mixture when fired at 1100°C. is shown in Fig. 1.

In practical enamel making, the only one of the four materials—i. e., antimony oxide, boric oxide, calcium and fluorine—that can be eliminated is calcium. The writer has found that under a given set of conditions, the tendency for oxide of antimony enamels to turn blue was lessened when the calcium in the mix was reduced. This meant the replacement of whiting or fluorspar by other fluxes. It is generally necessary to use cryolite to take the place of part of the fluorspar.

Tin Oxide. When enamelers of cast iron first began experimenting with oxide of antimony enamels, they found that when oxide of antimony and oxide of tin were used together, blue tints were produced. Since nearly all the formulae used in this country for cast iron contain calcium in some form, it is not certain whether this is a new color phenomenon or is due simply to an intensification of the blue color produced by calcium. On the other hand, it has been found possible to blend antimony and tin enamels after melting, without producing tints other than those expected from the enamels used in the mixture. The mixing must be done thoroughly or an unpleasant mottled effect is produced.

Heat Treatment. As stated above, antimony enamels are all tan colored in the first stages of the burn, and this color decreases in intensity as the smelting progresses. Enamels containing lead oxide have a yellow color component which is not effected by heat treatment. Calcium produces a blue color, which increases in intensity with duration of the smelting pro-

cess. The result of this combination of color effects is as follows: If a sample is drawn in the early stages of the smelting and cooled, it will be found to be a light tan if lead oxide is absent, and to be a tan enlivened by a mixture of yellow if lead oxide was used in the batch. As the heating progresses, the tan color will gradually fade, but the yellow due to lead oxide persists. If calcium is present in the composition, the blue color it produces is either not developed during the early stages of the burn, or is masked by the decided tan color. After long continued smelting, in the absence of both lead and calcium, the enamel gives a good white, but one of inferior opacity. If lead is present and calcium is absent, the white obtained will have a yellow tint, the intensity of which will depend on the amount of lead present. If calcium is present, the blue color developed thereby increases in intensity as the smelting proceeds and tends to neutralize the tan and yellow colors, producing whites or tints of green. Finally blue becomes the predominant color, giving enamels that range in hue from a faint greenish blue to a pronounced robin-egg blue.

The whites secured by neutralization of the tan and yellow tints by blue are more opaque than those secured by eliminating the tan color by long continued smelting, since the neutralization takes place at a comparatively early stage in the smelting, and therefore there is much less opportunity for solution of the opacifying agent in the glass. Since all antimony enamels are tan at the beginning of smelting, the problem of producing a good opaque white enamel is to so control the proportions of lead oxide and calcium or cobalt oxide, that the tan and yellow colors are neutralized by the blue, thereby producing a good white when the enamel is first thoroughly smelted. When it is remembered that any change in the composition of the enamel has a decided effect not only on the color, but on gloss, working properties, fit of the enamel to the iron and durability of the finished ware, it is obvious that the problem is not a simple one.

DARK SPECKS

The third difficulty encountered in the use of antimony enamels is that dark specks are likely to appear either near or

at the surface of the enamel. These vary from the size of a pin head down to microscopic size. Of course even a few of the larger sized specks disqualify a large piece of ware for sale as a high grade fixture. The specks are of two kinds; first, those that are entirely black, and second, those that have a black or dark brown center surrounded by a reddish-brown ring. The occurrence of the specks is quite erratic, varying widely in different batches of enamel made from the same formula and from the same raw materials.

The source of these specks have been attributed to many causes, mainly to impurities in one or other of the raw materials. Many attempts have been made by various enamelers to get rid of the specks by changing the composition of the enamel, or by securing raw materials from a new source. Owing to the spasmodic occurrence of the specks, some of these attempts seemed at first to be successful; but soon the specks would return as thick as ever. In fact, it is really surprising how much dirt can be incorporated into the raw batch of an enamel without noticeably affecting the appearance of the finished ware. Sometimes scrap enamel that contains enough sand, iron scale, etc., to render it decidedly gray in color will make, when remelted, cleaner ware than enamels made at the same time entirely from selected raw materials. Except in cases where external contamination by dirt was evident, the writer has never seen any specks of the kind under discussion in enamel frits before grinding. Equally significant is the fact that the specks do not occur in carefully conducted laboratory experiments. In making several hundred laboratory melts with commercial materials, we never found these specks in our trial pieces.

At various times, we have had occasion to examine under the microscope the specks in the antimony enamels from quite a number of different firms. We found that fully ninety percent of the specks could be divided into two groups. The first class consisted of black globular masses which were hollow, and often contained small particles of carbon. Evidently these were caused by the carbonization of small particles of combustible material while the enamel was being melted on the ware. The

specks in the second class were solid particles, either black or brownish black surrounded by a reddish-brown ring. These particles were decidedly magnetic, and when subjected to chemical test always showed the presence of iron. There is, therefore, no question but that they were due to contamination of the enamel with particles of metallic iron or the magnetic oxide of iron.

The cause, then, of the great majority of the dark specks in antimony enamels seems to lie in contamination of the enamel with external dirt after smelting. The particles causing the carbon spots may be small particles of wood from quenching tanks, mill covers, sieves, storage boxes, etc. On the other hand, they may be small specks of belt dressing or grease from the machinery used in the mill rooms and enameling rooms. The particles of iron and metallic oxide may come from the dryers, mills mechanical sifters, etc., or from the outside of the casting being enameled. In examining the enamel powder from several plants, we invariably found several or all of these foreign substances.

The objection that is always raised by manufacturers to the above analysis of the cause of the dark specks is that the specks do not appear in tin enamels made in the same manner and with the same equipment. The answer is that it can be easily demonstrated that the tin enamels contain exactly the same kind of particles and just as many of them. The difference is that the specks do not show up as prominently in the tin enamels. In the first place tin enamels are as a rule more opaque than antimony enamels, and hence any specks not actually at the surface of the ware are better hidden than in antimony enamels. In the second place, and much more important, is that fact that owing to differences in composition, the antimony enamels have a much stronger slagging action on the foreign particles, and the discoloration caused by the foreign particles spreads much further. The discoloration caused by a speck of foreign material in a tin enamel is practically the size of the particle. The discoloration caused by a similar particle in an antimony enamel may be six or eight times as large as the particle.

The obvious way to decrease the dark specks in antimony enamels is to use great care to keep them as free as possible from contamination. This is more easily said than done, however. In the first place, it is hard for even the man who makes the enamel to realize that the one essential requirements is absolute cleanliness. He is very likely to spend his energies in futile attempts to get rid of the dark specks by altering his formula or by securing some of his raw materials from new sources. Even more difficult is it to gain the confidence of the various workmen who handle the enamel, and without their hearty co-operation such a program will be more or less of a failure. In most cases, material decrease in the amount of contamination means more labor and changes in equipment, and consequently expenditure of considerable money. The men who hold the purse strings are liable to hold that the equipment and labor that always gave fairly clean tin enamels should be equally satisfactory for antimony enamels.

Moreover, a new conception of cleanliness must be instilled into the minds of all connected with the making and handling of the enamels. In most plants, the making and handling of the tin enamels was conducted in a manner that was fairly clean, as cleanliness goes in factories. To make a marked improvement in these long established shop methods means that every man concerned must make a distinct and sustained effort. Such effort is hard to obtain under the best of conditions and practically impossible when there is little enthusiasm for the project.

The results are that, while some attempt has been made in factories to reduce the amount of black specks by change in equipment and more cleanly methods, the project generally has been undertaken with some of those interested dubious of its value and with others openly or secretly opposed to it. The degree of success of the plan has, of course, been about in proportion to the enthusiasm and general support given it. Antimony enamels have been in use longer in Germany than in this country. The cleanest antimony enamel the writer has seen was made by a German manufacturer. This manufacturer informed me that, after several years of strenuous effort, he had been able

to inspire his shop organization with a general enthusiasm for cleanliness, and the results had been antimony enamels practically free from black specks. No doubt, American manufacturers will eventually travel the same road.

SUMMARY

Gloss. Oxide of antimony enamels of good gloss can be made from three types of formulae: first, the high boric oxide, no lead type; second, the medium boric oxide, no lead type; third, the low boric oxide, lead bearing type.

Color. Oxide of antimony enamels contain three color components: a tan, probably due to sulphur and fading as the smelting continues; a yellow, due to lead oxide and persistent; and a blue, due to a combination of antimony oxide, boric oxide, calcium and fluorine, which grows more intense as smelting continues. Opaque whites are produced by controlling the heat treatment and composition so that the tan and yellow are neutralized by blue.

The dark specks in oxide of antimony enamels are due to contamination with organic or metallic dirt after the enamel is smelted. The remedy is extreme cleanliness.

Ceramic Engineering Laboratories,
Iowa State College.

DISCUSSION

Mr. Silverman: I should like to ask Mr. Staley whether he tested the black spots for lead or tin; also as to whether he has any theory as to the nature of the antimony compound which is causing the opacity, that is, the nature of the reaction of the antimony with the other materials. Also as to his opinion as to the literature appearing in foreign publications against the use of antimony enamels for cooking utensils.

Prof. Staley: I would say that outside of a few experiments, I have never tried the use of any appreciable amount of tin in oxide of antimony enamels. There are as many specks in enamels which contain no lead as those which do, and that the mate-

rials are either carbon or if metallic at all, ninety-five percent of them will be attracted by a magnet. They must be iron.

As to the use of antimony enamels for cooking purposes, I would say that the question has been asked me several times, whether I would recommend the use of antimony compounds for cooking utensils in this country. I have always answered that I do not believe the profits justify taking the risk. I would rather make my money in some other way than taking chances on poisoning someone.

Mr. Silverman: Has it occurred to you that the antimony, which goes in, forms an acid radical, where you have a large amount of base in the flux?

Prof. Staley: It might. You have in enamels several strong acids, B_2O_3, SiO_2 and fluorine. In the presence of considerable quantities of these it would seem that the Sb_2O_3 would be neutral and would not enter into the reaction at all. The problem of making good enamels by any means whatsoever was so great that I never got around to doing very much experimental work on the purely theoretical side. Oxide of antimony is a great deal more difficult to use than oxide of tin, and since there was considerable technique that had to be worked out, practical problems had to take precedence over theoretical questions.

Mr. Silverman: Would not that be an interesting point? I have found recently in glasses that so much can be accounted for by a comparison with aqueous solution and suspension. I believe that the future of the glass business depends upon how much we can understand of what is going on. After all, a knowledge of composition and the nature of the materials in glass is going to govern our future work.

DENTAL PORCELAINS

BY ARTHUR S. WATTS

To the ceramist, the term porcelain brings to mind a body made up chiefly of clay with feldspar and quartz as the other principal constituents. The fluxing action of the feldspar is supplemented in many cases by small additions of calcium carbonate.

The mechanical requirements of most porcelains are stability against collapse during forming, against cracking during drying, and against deformation during the vitrifying process.

In the case of dry-pressed tiles, these requirements are not so severe, and in special wares with thin walls and overhanging edges the requirements are exceptionally severe. In the former case the clay content may be greatly reduced, and the feldspar and quartz content proportionately increased with an increase of translucency and an improvement of color. In the latter case the problem of insuring against deformation during vitrification without sacrificing the desired degree of translucency makes the composition a matter of delicate adjustment.

That porcelain is used for the manufacture of artificial teeth is known by every ceramist, but the particular type of porcelain employed in this industry and the peculiarities in its mode of preparation and manufacture are known to few. The apparent lack of interest displayed by ceramists is probably due largely to the difficulty of obtaining definite information on the subject, and the small amount of ceramic materials consumed.

There are several grades of porcelain employed in dental work. Their chief differences consist of the flux elements introduced and the temperatures of maturity.

For the manufacture of artificial teeth, a porcelain body which is claimed to have been in successful use for many years has the composition:

	percent
Ignition loss	2.50
SiO_2	68.17
Al_2O_3	16.72
TiO_2	.23
Fe_2O_3	trace
MnO	trace
CaO	none
MgO	none
K_2O	10.08
Na_2O	2.32
	100.02

Approximate mineral composition:

	percent
Feldspar	81
Clay substance	4
Flint	15

Chemical formula:

$$\left.\begin{matrix} .74\ K_2O \\ .26\ Na_2O \end{matrix}\right\} 1.14\ Al_2O_3 \left\{\begin{matrix} 7.830\ SiO_2 \\ 0.002\ TiO_2 \end{matrix}\right.$$

Another commercial dental porcelain body is said to consist of 80 percent feldspar and 20 percent quartz, fused together at cone 9 and then finely pulverized and mixed with 5 percent bone ash.

For dental inlays in which true porcelains are used, a wide variety of porcelains are employed. Some of these are almost as refractory as the porcelains of which the artificial teeth are made. Others are so fusible as to be correctly classed as enamels. The chief advantage of these low fusing bodies is that they can be matured in the ordinary dentist's furnace which cannot stand the temperature at which the best artificial teeth are fired. These inlay porcelains were formerly used by dentists for the manufacture of entire teeth or for the manufacture of porcelain

crowns, but the practice of inserting true porcelain inlays has been almost completely abandoned and for crown work an artificial tooth is ground down to fit the requirement.

These porcelains were supplied to the dentist in the form of powder. He mixes the powder with water and by a deft method of jarring the mold he causes the wet porcelain powder to completely fill it, the excess water coming to the surface.

The following analysis of a very refractory dental porcelain body which is marketed in powder form for the use of dentists is fairly representative of its class:

Chemical composition:

	percent
Ignition loss	1.84
SiO_2	71.10
Al_2O_3	12.12
TiO_2	.20
Fe_2O_3	.28
CaO	1.10
MgO	none
Na_2O	1.88
K_2O	11.30

Approximate mineral composition:

	percent
Feldspar	89.50
Sodium carbonate	4.00
Calcium carbonate	2.70
Flint	3.80
	100.00

Chemical formula:

$$\left.\begin{matrix} .70\ K_2O \\ .18\ Na_2O \\ .12\ CaO \end{matrix}\right\} \left.\begin{matrix} .700\ Al_2O_3 \\ .014\ Fe_2O_3 \end{matrix}\right\} \left.\begin{matrix} 6.840\ SiO_2 \\ 0.014\ TiO_2 \end{matrix}\right.$$

The proportions of soda, whiting and free flint would indicate that these were fritted into a glass of the following composition:

$$\left.\begin{matrix} .58\ Na_2O \\ .42\ CaO \end{matrix}\right\} 1.0\ SiO_2$$

This glass was subsequently mixed with the feldspar.

Such a glass would be slightly soluble in water, and on the drying of the molded porcelain the alkalies would tend to come to the surface, thus aiding in the development of a glassy surface. If the soda is added as sodium silicate, and the whiting added raw, this would certainly be the case.

A softer porcelain used for the same purpose as the preceding is found to have the composition:

	percent
Ignition loss	2.30
SiO_2	69.58
Al_2O_3	11.32
Fe_2O_3	.28
TiO_2	.16
B_2O_3	.30
CaO	2.40
MgO	none
Na_2O	1.74
K_2O	11.82

Approximate mineral composition:

	percent
Feldspar	61.06
Potassium carbonate	1.98
Sodium carbonate	1.98
Calcium carbonate	4.21
Borax	.83
Flint	29.07

Chemical formula:

$$\left.\begin{matrix} .638\ K_2O \\ .141\ Na_2O \\ .221\ CaO \end{matrix}\right\} \left.\begin{matrix} .565\ Al_2O_3 \\ .090\ Fe_2O_3 \end{matrix}\right\} \left.\begin{matrix} 5.900\ SiO_2 \\ 0.023\ B_2O_3 \\ 0.011\ TiO_2 \end{matrix}\right\}$$

A very soft porcelain enamel formerly much used for inlays, etc., has the composition:

	percent
Ignition loss	1.15
SiO_2	68.14
Al_2O_3	2.20
Fe_2O_3	none
TiO_2	trace
B_2O_3	10.60
CaO	.80
MgO	none
Na_2O	10.08
K_2O	6.94

Approximate mineral composition:

	percent
Feldspar	12.02
Sodium carbonate	7.90
Potassium carbonate	7.21
Borax	10.95
Calcium carbonate	1.43
Flint	60.49

Chemical formula:

$$\left.\begin{matrix} .295\ K_2O \\ .650\ Na_2O \\ .055\ CaO \end{matrix}\right\} .086\ Al_2O_3 \left\{\begin{matrix} 4.544\ SiO_2 \\ 0.706\ B_2O_3 \end{matrix}\right.$$

This produces a clear, highly fluid glass on fusion, and it is hard to see how a satisfactory porcelain could be produced from it without the addition of some viscous silicate. Nevertheless it was extensively and successfully used for many years.

The use of true porcelains for inlays has been almost completely replaced by so-called "artificial porcelains." These are not porcelains, according to the ceramic classifications, but merely silicate cements. The compositions of these cements are various. Chas. G. Voelker, D. D. S., of Brooklyn, N. Y., in his treatise

"The Rational Use of the Silicate Cements" read before the Ontario Dental Society, Ontario, Canada, February, 1914, throws much valuable light on the composition and properties of these silicate cements. He reports as follows:

"The modern oxy-phosphate cement consists of zinc oxide and ortho-phosphoric acid." Archer's New Artificial Enamel, patented by Professor Paul Steenboch, is composed principally of pure beryllium compounds. A basic solution of beryllium nitrate and sodium silicate forms a precipitate which is washed and calcined at red heat, forming 3 BeO—SiO_2. This is finely powdered and if additional strength is desired alumina or powdered glass is added. The powder is intimately mixed with 52 percent ortho-phosphoric acid in which aluminum phosphate (containing a small amount of zinc or strontium phosphate) is dissolved almost to the saturation point. The setting process is as follow: the acid liquid withdraws from the beryllium silicate its beryllium oxide content, leaving a hydrated silicate in which phosphates are present. Other compounds adaptable to this type of cements are beryllium oxide, aluminium oxide, zinc oxide, basic phosphates, borates, fluorides and silicates. Either simple salts or double salts of two or more metals may be used. In the original patent specification silicic anhydrid (or silicic acid) was also used and probably aided translucency.

Dr. W. V. B. Ames, who produced **"Berylite,"** which he calls "a siliceous cement" and also "a synthetic feldspar modified by rare earths" says "these silicate cements are all oxyphosphates, being compounds of modified phosphoric acid as the liquid element and powders capable of forming basic phosphates when incorporated with such a liquid." The powder used in **Berylite** consists of basic silicates of calcium and aluminium, aluminates and rare earths combined at so high a heat that an indescribably complex compound results."

Dr. Abraham, who discovered **"Translucin,"** says that the essential ingredient of all silicate cements is aluminium oxide which becomes more insoluble in water and acids when heated to 1500°C. and is almost infusible. If heated too high, Al_2O_3 cannot be used technically for cement powder and in order to control and lower its fusing and annealing point, he adds fluorides, which lower the temperature to about 1250°C.

Dr. Voelker shows that the silicate cements are by analysis composed of a powder having, as its main constituents, silicate of lime and alumina with admixtures of such other ingredients as lithium phosphate, sodium borate, free lime, aluminium oxide, silicate of beryllium and silicic acid. The liquids in all cases analyzed were modified solutions of phosphoric acid. He explains the difference between these silicate cements and Portland cement. Also between these ce-

ments and "true porcelains." In the latter case, he points out that "true porcelain" is developed by fusion, and that pulverized porcelain combined with a liquid containing phosphoric acid and allowed to set cannot produce "true porcelain." In closing this section of his paper, he warns the dental profession against referring to these "silicate cements" as "porcelains."

Dr. Voelker did not incorporate in his paper the quantitative analyses of any of the silicate cements referred to. As such an analysis may have an interest for some of our readers, the author has had a reputable silicate cement analyzed and submits the same herewith:

Powder:

	percent
Ignition loss	2.00
SiO_2	37.00
Al_2O_3	32.20
CaO	7.50
Na_2O	10.10
P_2O_5	1.90
F	9.30

Liquid:

Solid content .....41.50 percent

which consists of

	percent
Na_2O	6.00
P_2O_5	35.50

The powder is isotropic and possesses a uniform index of refraction which indicates that it has been fused and subsequently pulverized.

The author was impressed, in an extensive study of the feldspar mining industries of the United States, with the fact that in every district visited, the pioneer operations were undertaken by parties in search of feldspar for dental porcelains. The conclusion naturally reached was that feldspar in a high state of purity was required for this purpose. Also the fact was noted

that only the highest grades of potash feldspar were chosen for this class of work.

The fact that potash feldspar is found most satisfactory would be expected in view of the fact that its process of vitrification or fusion is gradual, extending through a deformation temperature range of about 30°C., whereas, that of soda feldspar or lime-soda feldspar does not exceed 10°C.[1] Furthermore, the degree of transparency of the potash feldspars is far greater than that of any soda or lime-soda feldspar commercially available. The quality and degree of transparency are almost as important as color in the duplication of natural teeth.

Through the courtesy of Mr. George H. Whitely, of the Dentists' Supply Company, of York, Pa., the author was permitted to study the processes of manufacture in detail.

The feldspar, which is the chief constituent of dental porcelain, is obtained in the crude form direct from the quarry. It is first crushed to about one-fourth inch size and hand sorted to remove discolored portions and any foreign material. The accepted portion is placed in drag mills of about thirty inches in diameter and ground to the desired degree of fineness. This has been found quite important as too fine pulverization is claimed to produce decreased transparency in the burned teeth, while too coarse pulverization raises the temperature of maturity and increases the wear on the furnaces.

The feldspar powder is then mixed in proper proportions with kaolin and quartz to give the desired shrinkage and mechanical strength in the finished product.

Owing to the low clay content, a small amount of starch and gum arabic or tragacanth is added, and these are found to aid materially in the perfect filling of the mold and the release of the tooth from the mold after drying.

Artificial porcelains are demanded in a great variety of colors to match natural teeth, and there are often several shades and tints in the same tooth. To meet these requirements the raw porcelain is made up in a variety of colors and tints, and these are blended in the process of molding the tooth. For obtaining

[1] Vol. XV, *Trans. Amer. Cer. Soc.*, p. 144.

these colors, iron, titanium, cobalt, copper, chromium, maganese, gold and many other oxides are employed.

The process of molding the tooth is as follows: The original model of the tooth is first produced in plaster of Paris of increased size to provide for shrinkage in burning. These models are made in two parts to permit the removal of the tooth from the mold produced. The mold is of bronze and is produced by molding and pouring in a manner similar to all bronze castings, but great care is necessary to insure the high degree of accuracy demanded.

The forming of the tooth is accomplished by laying into the mold a small amount of the light colored raw porcelain body at the point forming the biting edge of the tooth. The darker colored portion which constitutes the body of the tooth is then layed in over this. Each color of material is introduced by a separate operator, and these operators work in groups. The material is put into the molds with the finger, and when the two half molds are filled they are placed together immediately, and securely clamped to insure a union of the body of the tooth. The mold is then subjected to heat and pressure which bakes the tooth into a tough mass which has shrunk only very slightly and resembles a very soft biscuit porcelain. The teeth are rapped out of the mold, and the burr edges produced by the joint in the mold are carefully removed by a file, and these edges polished.

The teeth are now ready for burning, which is one of the most delicate steps in the manufacturing process. The biscuited teeth are carefully placed in an inverted position in fused silica trays. Those which will not conveniently remain in this position are slightly impressed into a thin layer of quartz powder placed in the bottom of the tray. The tray is placed in a gas muffle furnace and heated to the required temperature. The shortest possible heat treatment is desired for the firing of the teeth, since the surface must become fused and smooth without the heat so penetrating the mass of the tooth as to cause it to deform in any degree.

As the tooth is of practically the some composition throughout and no glaze is applied, the regulation of this firing process

is very important. The burner allows the tray of teeth to remain in the heat of the furnace until he can observe the development of the brilliant surface due to fusion. The tray is then removed and carefully inspected by the light of a large gas flame to make certain of the proper surface texture. If unsatisfactory the tray is returned to the furnace. If satisfactory, the tray is placed in an annealing oven which is directly above and is heated by the waste heat of the furnace. After annealing, the teeth are cooled and graded to eliminate any imperfect specimens.

For attaching the teeth to the rubber plate, or for crowns, the teeth must be equipped with metal pins. These are usually of platinum. They are made like a short pin with a flat point and a round head. When of platinum they are placed in two small holes in the base of the biscuit tooth, and are baked with the teeth.

When the pins are of some base metal or have base-metal cores they are placed in the teeth after the firing and are soldered to platinum anchorages which have been previously placed.

The temperature at which the porcelain must be fired precludes the use of any metal but platinum, if the pins are to be fired with the teeth. If they are placed in the teeth after firing and are fused in at a lower temperature, a lower fusing metal may be used.

Attempts to develop a practical dental porcelain at a temperature at which a cheaper pin can be employed have not met with success. With the increased knowledge of fusion behavior of ceramic mixtures, which has been made available in recent years, this would not appear to be a difficult problem, and would make a profitable line of investigation for some ambitious ceramist.

THE USE OF BARIUM FLUORIDE FOR THE PREVENTION OF DRYER SCUM ON BRICKS

BY HOMER F. STALEY

Barium carbonate has been used for a long time to prevent scum forming on bricks during drying. The objections to its use are first, its rather high price, second, its limited solubility, and third, its tendency to lighten the color of the brick if used in excess, since this excess does not readily fuse into the matrix of clay. Barium chloride is dangerous to use, for any excess produces a scum in and of itself. Lovejoy[1] has suggested the use of the acid carbonate and the hydroxide. These are more soluble than the normal carbonate but would cost about the same for unit weight of barium, and any excess might cause a scum of its own.

Barium fluoride is produced in limited quantities in this country as a by-product in the manufacture of hydrogen peroxide by the barium peroxide method. Having used the fluoride in large quantities in other lines of work, and knowing something of its properties, and that it could be bought for about a third of the price of the carbonate, we performed some simple experiments to determine its efficacy as a preventive of dryer scum in bricks.

While there are many salts that may form dryer scum, the efflorescence caused by many of these is either volatilized during the burning process or fused into the surface of the ware, thus losing its discoloring power. The two salts commonly causing scum are the sulfates of calcium and magnesium. In Table I is given a tabulation of the chemical reactions and solubilities involved in precipitating these two salts with barium carbonate and fluoride.

In attempting to produce efflorescence by adding calcium sulfate and magnesium sulfate to a fine grained red burning shale, we found that even with slow drying no scum was produced by additions of $CaSO_4.2H_2O$ up to three percent of the dry weight of the clay. This same failure to produce scum by means of cal-

[1] *Trans. Amer. Cer. Soc.*, Vol. VIII, p. 255.

cium sulfate is recorded by Barringer[2]. On the other hand. in our work one percent of $MgSO_4 \cdot 7\,H_2O$ gave a copious amount of scum, and a mixture of one-half percent of the magnesium sulfate with one-half percent of the calcium sulfate produced even more pronounced efflorescence, the magnesium salt seeming to bring out the calcium salt along with it. This decided difference in scum forming power between the two sulfates seems to be due to the greater solubility of the magnesium sulfate and, probably as

TABLE I—SOLUBILITY AND CHEMICAL RELATIONS OF THE SALTS INVOLVED IN SCUMMING AND ITS PREVENTION

Parts water to dissolve one part of salt.....	495		45,450		435,000		77,000
Reaction.....	$CaSO_4$	+	$BaCO_3$	⇄	$BaSO_4$	+	$CaCO_3$
Formula weights.....	136.14		187.37		233.44		100.07
Parts water to dissolve one part of salt.....	3.75		45,450		435,000		9,400
Reaction.....	$MgSO_4$	+	$BaCO_3$	⇄	$BaSO_4$	+	$MgCO_3$
Formula weights.....	120.39		197.37		233.44		84.32
Parts water to dissolve one part of salt.....	495		614		435,000		62,500
Reaction.....	$CaSO_4$	+	BaF_2	⇄	$BaSO_4$	+	CaF_2
Formula weights.....	136.14		175.37		233.44		78.07
Parts water to dissolve one part of salt.....	3.75		614		435,000		13,000
Reaction.....	$MgSO_4$	+	BaF_2	⇄	$BaSO_4$	+	MgF_2
Formula weights.....	120.39		175.37		233.44		64.32

a result of this, the fact that magnesium sulfate slows down the drying of the clay while calcium sulfate hastens the drying. The writer has shown the effect of these two salts on the rate of drying of this clay at another place in this volume.[3]

Of course the amount of efflorescence obtained from a given amount of soluble salts and the amount of precipitant necessary to overcome the scumming depends on the chemicals and the clay used, and the rate of drying. In our work it was found that

[2] *Trans. Amer. Cer. Soc.*, Vol. IV, p. 224.
[3] Page.

when large amounts of soluble salts were present, it was not necessary to add the amount of precipitants theoretically necessary to convert all the soluble salts into insoluble ones. For instance, when two and a quarter percent each of $CaSO_4$ (plaster of Paris) and $MgSO_4.7H_2O$ were added, the theoretical amounts of precipitant were five percent of $BaCO_3$ or four and a half percent of BaF_2. We found that the scum was absent in samples containing three percent of either of these salts. On the other hand, when one-half percent each of $CaSO_4.2H_2O$ and $MgSO_4.7H_2O$ were present, the scum disappeared when one percent of either $BaCO_3$ or BaF_2 were added. In this case, practically theoretical amounts of precipitants were necessary.

In not one of a half dozen trials did we find it necessary to use an excess of precipitant, which is contrary to the usual experience. It must be remembered, however, that we calculated the theortical amount of precipitant from a known addition of soluble sulfates to a clay, while in shop practice the soluble sulfates must be determined by analysis. Owing to absorption, analytical determination of soluble sulfates will likely give results that are too low. As stated above, circumstances have a decided effect on the production of scum, and with a different clay or different rate of drying, we might have obtained different results.

It was expected that the scumming would be corrected by smaller amount of barium fluoride than of barium carbonate, on account of the much greater solubility of the fluoride. The fact that equal weights were required seems to indicate that the salts entered into reaction to an equal extent. Since these salts are nearly equivalent chemically, weight for weight, the effects produced were about the same. As nicely explained by Lovejoy, the initial solubilities of the reacting salts have little to do with the completed chemical reaction, provided opportunity is given for progressive solution of the more insoluble salt.

Aside from the question of cost, it is not feasible in some cases of bad scumming to use barium carbonate as a corrective since large amounts of it, as a whole, lighten the color of a red burning clay. This was quite evident in our work. On the other

hand with excess of BaF_2, the only effect on the color was a slight darkening due to slightly increased vitrification caused by the fluxing action of the fluoride.

In those cases where an excess of barium fluoride was used, the scum, presumably of BaF_2, was noticeable on the samples when they came from the dryer, but this disappeared entirely during the burning. All the samples in which an excess of BaF_2 was used were a good clear red when burned. Evidently the scum was either volatilized or fused into a colorless glass and absorbed into the clay during burning. This would be expected from the fusible nature of BaF_2. Because it does not produce a scum when used in excess, BaF_2 has an advantage over the other soluble salts of barium that have been suggested for use, namely, the chloride, hydroxide, and acid carbonate. In fact, there is reason for believing that the addition of soluble and fusible salt to a clay is a possible method of overcoming scum in some cases. While investigating the effect of salts on the rate of drying of clays, the writer added sodium chloride to a shale that scummed when dried slowly. The time taken for drying was much lengthened by the addition of the salt, and the dried samples all showed scum, which was heaviest on those containing the largest additions of salt. After burning, the samples to which no sodium chloride had been added were badly scummed while those to which it had been added were free from scum. Evidently the fusible salt had fluxed the infusible ones.

The effect of the barium fluoride was to increase the vitrification slightly at all temperatures. This was to be expected from the fusibility of both the fluoride added and of those formed by neutralization of the soluble salts in the clay. No puffing due to the formation of gaseous silicon or iron fluorides was encountered. This is easily accounted for since the amounts of fluorides added were small, and any iron or silicon fluoride formed would probably be given off at low temperature while the clays were still quite porous.

Some of the samples of barium fluoride we have examined contained a very slight excess of hydrofluoric acid. Since this would have an injurious effect on the machinery used in the

manufacture, it would have to be neutralized. This could be done in a simple manner by adding to the tank in which the fluoride was being agitated or dissolved either calcium carbonate (limestone), soda ash, or barium carbonate. The first material would be the cheapest, but, considering the effect on the clay of the fluorides formed, the last would be the best. The amount required would be very small and the expense inconsiderable in any case. Neutralization is complete when bubbles cease to be formed on addition of carbonate. The carbonate should be stirred up with a little water before it is added to the mixer, since any lumps of the dry powder would be liable to contain air, the bubbles from which could not be distinguished from those of CO_2 caused by the neutralization.

We may summarize the advantages of barium fluoride for use as a preventive of scum in place of the other salts of barium that have been proposed as follows:

1. It is less expensive.
2. It is more soluble than barium carbonate.
3. The amounts required are the same or less.
4. It has no deleterious effect on the color of the burned ware.
5. An excess does not produce a scum.
6. It promotes vitrification.

There would be one slight inconvenience in the necessity for neutralizing a small amount of free acid in some lots of BaF_2.

Incidentally we have suggested that it is possible to stop efflorescence in some cases by adding any salt that forms a fusible scum.

Ceramic Engineering Laboratories,
Iowa State College.

A COMPARISON OF COSTS PER SAGGER OF BISCUIT AND GLOST KILNS, ALSO OF KILN EXPENSE

BY THOMAS GRAY

The following paper is largely of importance in comparing the different methods of arriving at kiln costs.

The figures ascribed to Mr. Mayer are taken from Vol. II, page 160 and Vol. III, page 193, *Trans. Amer. Cer. Soc.* My figures are taken from Vol. IX, page 785, *Trans. Amer. Cer. Soc.* and from notes made since then. The figures ascribed to Mr. Clark are from memoranda found after his decease in 1896. I have taken Mr. Clark's figures just as I found them, and without examination, since I have generally found him to be accurate in figuring such matters. I might also state that Mr. Mayer makes no statements, unless he is confident of their accuracy.

Both Clark and Mayer use the cubical content method of estimating costs. I regret to state, however, that they are wide apart as to the cubical contents of saggers. I have adopted the square inch method for each bung, getting the cost per sagger from the number usually in each bung. I may not treat myself fairly, because the square inch content of an oval, as I figured it, is more than it really contains.

The itemized expense figures for both biscuit and glost kiln as here given for Mayer are not his figures. I had to take his totals and apportion the items of expense as best I could, and therefore, some may be out of proportion. I was further handicapped by the fact that Mr. Mayer does not give the dimensions of his saggers, and I have been obliged to make my calculations on the basis of my sizes—as far as I could. It may be that Mr. Mayer's saggers are of an enormous size, since the cubical content of his saggers in some cases are double Mr. Clark's figures. The sagger measurements I give are outside to outside.

The size of his kilns I have placed at 18 feet in diameter, judging from its cubical contents. Mr. Mayer's expense totals

are amazingly small, particularly so for the biscuit kiln. I hope that in the process of readjusting Mr. Mayer's figures I have done him no injustice; I wanted to make this study accurate, and having committed myself without looking fully into the subject, I had to go on with it as best I could.

This study indicates that a large kiln is more economical than a small one. It also indicates differences in costs due to differences in geographical positions.

TABLE I—BISCUIT KILN EXPENSE

	Clarke, 1893 17.5 feet diam.	Mayer[1], 1900 supposed diameter 18 feet	Gray, 1904 15.5 feet diam.
Placing	52.75	40.00	40.35
Preparing, firing, wheeling coal and ash	9.00	7.85	9.00
Drawing	27.00	12.50	28.08
Wad, clay and labor (Mayer clay only)	14.25	2.25	6.00
Fuel	76.50	20.45	45.25
Sand	.75	.50	1.00
Loss on saggers	15.00	These	13.36
Loss on clay ware	.....	items	2.00
Loss on biscuit ware	.....	estimated	35.00
Cost per kiln	$195.25	$83.55	$180.04

[1] Items of Mayer account are estimated to fit his total.

Anyone taking the full diameter of a kiln as placing capacity makes a mistake. In the old style kiln the bags must be taken into account, and there is much space also lost in the use of saggers.

A kiln 15½ ft. diameter contains	188.69 sq. ft.	= 27171 sq. in.
Less 9 bags, 1 ft. by 3 ft.	27. sq. ft.	= 3888 sq. in.
	161.69 sq. ft.	= 23283 sq. in.

This is the placing capacity of the kiln, but the saggers leave much waste space. My kiln holds 88 bungs of common oval saggers at 225½ sq. in. each, totalling 18716 sq. in. which I take as the available placing capacity.

TABLE II—COST OF FIRING BISCUIT SAGGERS

	Clark, 1893			Mayer, 1900		Gray, 1904				
Kiln capacity	2718566 cu. in.			2547701 cu. in.		18716 square inches				
Total cost of firing.	$195.25			$83.55		$180.04				
Cost per cu. in.....	.00718 cents			.003279 cents		.962 cents per square inch				
TYPE OF SAGGER	DIMENSIONS INCHES CIRCUMFERENCE X HEIGHT	CONTENTS CU.IN.	COST PER SAGGER CENTS	CONTENTS CU. IN.	COST PER SAGGER CENTS	DIMENSIONS—INCHES LENGTH X DIAMETER X HEIGHT	SURFACE AREA SQ. IN.	COST PER BUNG DOLLARS	NUMBER OF SAGGERS IN BUNG	COST PER SAGGER CENTS
Coffin, cup	51.50x 3.50	577	4.00	709	3.80	21.00x12.0x 4.50	252.00	2.42	42	5.76
Coffin, small	49.00x 6.50	975	7.00	....	....	20.50x11.0x 7.50	225.50	2.17	27	8.00
Coffin, large	51.50x 6.50	1073	8.00	....	....	21.00x12.0x 9.00	252.00	2.42	22	11.10
Basin, 9	51.50x 8.00	1320	9.50	1901	10.20	18.00 dia. x 7.00	254.50	2.44	28	8.71
Basin, 12	49.00x 7.50	1125	8.00	....	....	.....	.....	....	..	....
Chamber, 12	45.50x 6.00	776	5.50	1843	10.00	.....	.....	....	..	....
Coffin, cup	51.50x 3.50	577	4.00	709	3.80	20.50x11.5x 4.50	236.00	2.27	42	5.40
Score or jack	.....	....	....	1305	7.00	20.50x11.5x 5.50	236.00	2.27	38	5.97
Bed pan	51.50x 6.00	990	7.00	1305	7.00	20.50x11.5x 6.50	236.00	2.27	30	7.57
Common oval	51.50x 6.50	1073	8.00	1886	10.00	20.50x11.5x 7.50	236.00	2.27	27	8.40
Common oval, qts..	51.50x 8.50	1408	10.00	....	....	20.50x11.5x 8.75	236.00	2.27	23	9.87

TABLE II—Continued

	Clark, 1893			Mayer, 1900		Gray, 1904				
Kiln capacity	2718566 cu. in.			2547701 cu. in.		18716 square inches				
Total cost of firing.	$195.25			$83.55		$180.04				
Cost per cu. in.....	.00718 cents			.003279 cents		.962 cents per square inch				
TYPE OF SAGGER	DIMENSIONS INCHES CIRCUMFERENCE X HEIGHT	CONTENTS CU.IN.	COST PER SAGGER CENTS	CONTENTS CU. IN.	COST PER SAGGER CENTS	DIMENSIONS—INCHES LENGTH X DIAMETER X HEIGHT	SURFACE AREA SQ. IN.	COST PER BUNG DOLLARS	NUMBER OF SAGGER IN BUNG	COST PER SAGGERS CENTS
Common oval, 3 pts.	51.50x10.00	1650	11.90	....	....	20.50x11.5x 9.75	236.00	2.27	22	10.32
Common oval, 16 in.	53.00x10.50	1838	13.50	....	....	.....	.....	....	..	....
Cuspidor	.....	....	....	....	....	12.50 dia. x13.75	122.75	1.18	16	7.37
Ewer, 9	41.50x13.50	1458	10.50	2837	15.33	17.25x 9.5x13.00	164.00	1.57	16	9.81
Ewer, 12	38.50x13.00	1203	8.40	....	....	.....	.....	....	..	....
Jug, 6	41.50x11.00	1188	8.50	....	....	17.00x10.0x12.00	170.00	1.63	19	8.58
Nappie, 10	38.25x 5.50	500	3.60	....	....	.....	.....	....	..	....
Nappie, 11	41.50x 6.50	702	5.00	....	....	14.5 dia. x 7.0	165.17	1.58	30	5.27
Plates, 7	32.50x 6.50	429	3.00	....	....	12.5 dia. x 7.5	122.75	1.18	27	4.37
Plates, 8	35.50x 6.75	527	3.75	1045	5.60	13.5 dia. x 7.5	143.00	1.37	27	5.07

Kiln capacity:

Clark, 2,718,566 cubic inches; cost 0.00718 cents per cu. in.
Mayer, 2,547,701 cubic inches; cost 0.003279 cents per cu. in.

Memorandum by Mr. Mayer is made to the effect that the average loss of biscuit kiln is four percent, and that his kiln holds 75 assorted bungs.

Gray, 18716 sq. in. cost $180.04 = .962 cents per sq. in.

The computation for glost saggers is a little more complicated on account of the numbers and styles of saggers, but is carried out on the same basis as the biscuit kiln. I have not included all styles such as clover leafs, yokes, *etcetera,* but those I give will be enough to show my point.

Glost kiln expense on the basis of cubical and square inch content are as follows:

Clark, 1,946,728 cubic inches at 0.1122 cents per cu. in.

Mayer, 2,811,054 cubic inches at 0.005412 cents per cu. in.

Gray, 18716 square inches at $229.24 equals 1.225 cents per square inch.

Mr. Mayer, Vol. II, p. 164, says to add to cost of materials used, the cost of fritting. Cost of glaze at 6.7 percent equals 3.75 cents per pound.

TABLE III—GLOST KILN EXPENSE

	CLARKE, 1898 15.5 FEET	MAYER, 1900 SIZE UNKNOWN	GRAY, 1904 15.5 FEET
	dollars	*dollars*	*dollars*
Placing	42.40	35.00	42.50
Preparing, firing, wheeling coal and ash, etc	9.00	10.25	8.00
Drawing	25.00	22.00	28.00
Wad clay and labor	11.00	3.00	6.03
Fuel	61.25	27.00	33.25
Stilts and pins	11.50	.....	10.00
Loss on saggers	15.00	.....	17.50
Dipping, brushing and labor	23.25	19.00	18.00
Glaze and bitstone	20.00	.....	9.46
Glost warehouse expense, dressing, housing and packing	.....	36.00	26.50
Loss on glost ware, 3 percent	.....	.....	30.00
Totals	218.40	152.25	229.24

TABLE IV—COST OF FIRING GLOST SAGGERS

	Clark, 1893			Mayer, 1900		Gray, 1904				
Size of kiln	15½ ft.			18 ft. (Est.)		15½ ft.				
Capacity of kiln....	1946728 cu. in.			2811054 cu. in.		18716 square inches				
Total cost of firing.	$218.40			$152.25		$239.24				
Cost per cu. in.....	.01122 cents			.005412 cents		1.225 cents per square inch				
TYPE OF SAGGER	DIMENSIONS INCHES CIRCUMFERENCE X HEIGHT	CONTENTS CU.IN.	COST PER SAGGER CENTS	CONTENTS CU. IN.	COST PER SAGGER CENTS	DIMENSIONS—INCHES LENGTH X DIAMETER X HEIGHT	SURFACE AREA SQ. IN.	COST PER BUNG DOLLARS	NUMBER OF SAGGERS IN BUNG	COST PER SAGGER CENTS
Banjo, old, 5.....	.....	....	.....	2688	14.50	18.00x 9.50x9.50	171.00	2.09	22	9.50
Banjo, 6	48.0x 4.50	1368	15.50	1834	10.00	20.00x11.00x9.50	220.00	2.70	22	12.50
Banjo, 7	52.0x 9.50	1605	18.25	....	.....	20.75x11.50x9.50	238.00	2.92	22	13.25
Baker, 3	.....	....	.....	....	.....	14.50x11.25x9.50	163.50	2.00	22	9.00
Dish, 3	.....	....	.....	....	.....	14.75x11.00x9.50	162.00	1.98	22	9.00
Coffin, cup	49.0x 3.50	525	8.80	....	.....	20.25x11.00x7.50	223.00	2.73	26	10.50
Coffin, small cup ..	.....	....	.....	....	.....	20.25x11.00x4.50	223.00	2.73	42	6.50
Coffin, score or jack	.....	....	.....	....	.....	20.25x11.00x5.50	223.00	2.73	33	8.25
Coffin, small	49.0x 6.50	....	.....	....	.....	20.25x11.00x7.50	223.00	2.73	26	10.50
Coffin, large	51.5x 6.50	1073	12.00	....	.....	21.00x12.00x9.00	252.00	3.09	23	13.50
Coffin, large	.....	....	.....	....	.....	21.00x12.00x8.00	252.00	3.09	24	13.00

9's chamber covers.	.....	....	.....	....	.....	21.00x11.50x9.50	241.50	2.96	22	13.50
Common oval	51.5x 6.50	1073	12.00	1886	10.20	20.50x14.50x7.50	297.50	3.55	26	14.00
Common oval cup ..	.....	....	.....	709	3.60	20.50x14.50x4.50	297.50	3.55	42	8.00
Common oval low jack	.....	....	.....	1305	7.00	20.50x14.50x5.50	297.50	3.55	32	11.00
Common oval bed pan	51.5x 6.00	990	11.25	....	.....	20.50x14.50x6.50	297.50	3.55	30	12.00
Common oval, qts..	51.5x 8.50	1403	16.00	....	.....	20.50x14.50x8.75	297.50	3.55	21	17.00
Common oval, 3 pts.	51.5x10.0	1650	18.75	....	.....	20.50x14.50x9.75	297.50	3.55	20	17.75
Common oval, 16 in.	53.0x 6.50	1838	21.00	....	.....	.....	.....	....	..	.....
Basins, 9	.....	....	.....	1901	10.33	16.50 diam.x 7.50	214.00	2.62	26	10.00
Basins, 12	45.0x 7.00	885	10.00	....	.....	15.5 diam.x 7.50	188.00	2.30	26	9.00
Cuspidor	35.0x15.00	1140	12.80	2095	11.33	12.5 diam.x12.75	122.75	1.51	15	10.00
Dish, 8	.....	....	.....	....	.....	14.00x11.0x 9.00	154.00	1.89	23	8.00
Dish, 12	51.5x 7.00	1155	13.00	....	.....	18.50x14.0x 9.00	259.00	3.18	23	13.75
Dish, 14	53.0x 7.00	1228	13.75	....	.....	21.00x14.0x 9.00	294.00	3.61	23	15.67
Ewer, 9	41.5x13.50	1350	15.00	2837	15.33	17.00x10.0x13.25	170.00	2.08	16	13.00
Ewer, 12	38.5x12.00	1110	12.50	....	.....	15.50x 9.0x12.50	139.50	1.71	16	10.75
Fruit saucer	44.0x 9.50	1149	13.00	1909	10.33	12.50x12.5x 9.50	156.50	1.92	22	8.67

TABLE IV—Continued

	Clark, 1893			Mayer, 1900		Gray, 1904				
Size of kiln	15½ ft.			18 ft. (Est.)		15½ ft.				
Capacity of kiln....	1946728 cu. in.			2811054 cu. in.		18716 square inches				
Total cost of firing.	$218.40			$152.25		$229.24				
Cost per cu. in.....	.01122 cents			.005412 cents		1.225 cents per square inch				
TYPE OF SAGGER	DIMENSIONS INCHES CIRCUMFERENCE X HEIGHT	CONTENTS CU.IN.	COST PER SAGGER CENTS	CONTENTS CU. IN.	COST PER SAGGER CENTS	DIMENSIONS—INCHES LENGTH X DIAMETER X HEIGHT	SURFACE AREA SQ. IN.	COST PER BUNG DOLLARS	NUMBER OF SAGGERS IN BUNG	COST PER SAGGER CENTS
Jug, 6	41.5x10.00	1080	12.25	....	.....	17.50x10.0x11.50	175.00	2.14	17	12.33
Jug, 30	.....	....	.....	....	.....	17.25x10.0x 7.25	172.50	2.10	29	7.25
Nappies, 10	36.0x 5.75	466	5.20	....	.....	.....	.....	....	..	.....
Nappie, 11	38.5x 6.00	558	6.20	....	.....	14 diam.x 7.00	154.00	1.89	28	6.75
Nappie, 12	.....	....	.....	....	.....	16 diam.x 8.25	201.00	2.46	24	10.25
Plates, 5	41.0x 9.00	945	10.60	1567	8.40	17.50x 9.5x 9.25	166.50	2.04	22	9.25
Plates, 6	.....	....	.....	....	.....	19.50x10.5x 9.00	205.00	2.51	23	11.00
Plates, 7	.....	....	.....	....	.....	20.00x11.0x 9.00	220.00	2.70	22	12.50
Plates, 7	.....	....	.....	....	.....	21.00x12.0x 9.75	252.00	3.09	20	15.50
Plates, 8	36.0x 9.00	729	8.25	1045	5.60	13 diam.x 9.50	132.75	1.63	22	7.33

Having ascertained the cost of firing biscuit and glost saggers, the dead expense for the year should be figured and divided pro rata by the number of kilns produced, and considered as so much per cubic inch or square inch, as the case may be, making the cost of the ware as in my case: biscuit kiln $180.04; glost kiln $229.04; dead expense $187.50.

As an illustration of finding the cost of glost ware per sagger per dozen: I find in one instance a common oval bed pan sagger costing to fire twelve cents and holding the following:

TABLE V—COST OF CONTENTS OF GLOST SAGGER

		cents	*cents per dozen*
2 Nappies	10 in.	7.33	45
1 Nappie	9 in.	2.00	24
1 Dish	6 in.	0.67	8
1 S. D. bowl	36's	0.33	4
2 Tulip bowls	30's	0.67	4
14 Individual butters	...	0.33	1
2 Hd. cups		0.67	8
		12.00	

Under different combinations of placing, different costs may be found, but this is about where the costs would be and makes a good basis on which to work for cost prices.

Although it was not essentially a part of my paper I will include a memorandum of Mr. Mayer's idea of what belongs to "dead" expense, and also my view on the question. A study of the itemized kiln expense will show that Mr. Mayer does not include items that both Clark and myself consider properly belong there. He has placed them in his dead-expense list. He considers a plant producing 80 kilns a year would cost about $18,000 or $225.00 per kiln, while I would put it about $15,000 or $187.50 per kiln.

Mr. Mayer's dead-expense account includes the following:

Insurance on factory, stock, boiler, employers' liability.

Taxes and water.

Steam heating and lighting.

Repairs and tool account.
Office salaries, watchman and fireman.
Advertising, stationery and supplies.
Interest on capital.
Modelling.

My dead-expense account includes:

Office salaries and foreman.
Watchman and engineer.
Mold maker and plaster.
Taxes and expense account including insurance.
Water and lights.
Boiler and stove fuel
Repairs, teaming.
Rents and yard labor.

THE VALUE OF SPECIFIC GRAVITY OF RAW MATERIALS

BY D. E. HUMPHREY

Few clay manufacturers seem to appreciate the value in the use of simple specific gravity methods in determining the weight per cubic yard or cubic foot of raw material, or its use in giving a clue to the quality of different parts of the bank.

It is often difficult to pick out the objectionable parts of a shale bank by observation. If the specific gravity of a lump from a certain strata is much greater than the specific gravity of other parts of the bank, it is a good plan to burn a few lumps of both kinds to ascertain their qualities under fire. The appearance in the bank is often quite similar. I have seen the specific gravity vary from 2.46 to 2.63 in a six foot vein of clay, with a marked difference in the firing qualities of the two extremes. It may show that a certain stratum in the bank does not possess the qualities to be desired in the pavers or whatever is being manufactured. Such information enable one to tackle more intelligently the problem of working in the objectionable part of the shale or clay supply in such a way that it will do no harm to the quality, or, if necessary of eliminating the objectionable part entirely.

The weight of a cubic yard of bank may be closely estimated by multiplying the weight of a cubic yard of water (1684.8 pounds) by the average specific gravity of the bank. If the weight of a cubic yard of bank is known, blast holes may be located with greater assurance of securing good results. Good blasting generally brings down about four tons of shale for each pound of dynamite. Of course, this amount varies in different shale banks according to the blasting qualities of the shale. If the weight per cubic yard of the material to be blasted, the number of pounds of explosive per lineal foot of hole, and the number of tons of shale that can ordinarily be blown down with a pound of explosive are known, the location of blast holes becomes more or less a mathematical problem. Money may be saved by

securing this information and occasionally making the calculation to check up the blasting in the shale pit.

The weight of a cubic yard of shale divided by the average weight of a dry brick from the dryer will give the number of brick per bank yard. This enables one to estimate the number of brick in the shale bank or in the shale storage. We have all seen companies who would probably have spent their money differently, if they had accurately estimated the number of brick in the shale or clay supply.

The weight of a cubic foot of loose quarried shale is essential in haulage calculations and storage construction. When you buy a dinky locomotive, you ought to know the percent grade in the track, the number of cars to be hauled, the weight of the car and the weight of the load to be put on the car. For brick yard tracks, it is safe to figure 40 pounds draw bar pull for each ton to be hauled on the level, with an additional 20 pounds per ton for each one percent of grade.

One way to estimate the weight of the loose shale is to guess at it, or ask somebody, or look it up in a hand book. A better way is to calculate the weight by specific gravity. Weigh a tub, or some similar water-tight receptacle, on a platform scale. Fill the tub even full of the shale and weigh it, taking care to have the same proportion of coarse and fine shale that goes into the car or storage, and as nearly as possible, the same number of voids. Subtract the weight of the tub from the weight of the tub and the shale, and the result will be the weight of the shale. Now empty the tub, and fill it with water. Weigh the tub full of water. Subtract the weight of the tub from the weight of the tub full of water, and the result will be the weight of the water. Divide the weight of the water by the weight of one cubic foot of water (62.4 pounds). The result will be the number of cubic feet in the tub. Now divide the weight of the tub full of shale by the number of cubic feet in the tub, and the result will be the weight per cubic foot of loose quarried shale. This method applies equally well to ground clay.

The specific gravity of a lump of clay may be easily determined with a spring balance. Suspend the lump from the scale

hook and weigh it in air. Then weigh it in water. Subtract the weight of the lump in water from the weight of the lump in air, and the result will be the weight of the water displaced by the lump. Divide the weight of the water displaced by the lump by 62.4, and the result will be the fraction of a cubic foot of bank measure the lump occupies. Now divide the weight of the lump in air by the fraction of a cubic foot of bank measure which the lump occupies, and the result will be the weight per cubic foot of bank measure of the particular material in this lump. These are old methods that most of us have learned in our days of high school science.

On most brick yards, it appears that specific gravity is so old a topic, that it has been entirely forgotten. It pays sometimes to revive in our minds the old, simple fundamentals.

A card in a reference index which has on it the weight of a cubic yard of the bank; the weight per cubic yard of quarried shale, loosely packed as in the car; the weight of a cubic yard of quarried shale well packed as in the shale shed; the weight of a cubic foot of ground shale loosely packed as in the feeder bin; and the weight of a cubic foot of ground shale well packed as in the storage bin will be a comfort and satisfaction to the man, who is operating a brick yard and who has improvements to make.

Another card with the specific gravity of various parts of the bank, with a note as to how each acts when burned, may be of assistance in the everlasting fight for quality.

NOTE ON THERMO-ELECTRIC PHENOMENA OBSERVED IN SOME SILICATES[1]

BY A. V. BLEININGER, PITTSBURGH, PA.

It is a well known fact that two different aqueous solutions of inorganic salts show a difference in electrical potential at the boundary surface. Likewise, two different concentrations of the same salt in solution will show a potential difference. Lord Kelvin comes to the conclusion that differences in potential are also to be found at all boundaries of different substances or the same substances which show differences in temperature. In this connection attention need only be called to the Peltier effect in which heating of junctions takes place independent of the regular electrical heating effect.

These considerations caused the writer to wonder what differences in potential might be found by heating different silicates in contact with each other so as to form couples.

For this purpose four silicate mixtures of zinc oxide, manganese oxide, copper oxide, and ferric oxide were prepared. Flint passed through a 200 mesh sieve was used for the silica, and this was thoroughly ground with the metallic oxides to form the composition $RO \cdot 2SiO_2$. These mixtures were moistened, formed into lumps and were calcined to about cone 10. The heated materials were then again ground and recalcined to the same temperature. From the powder, small specimens (approximately ½ in. by ½ in. by ¼ in.) were molded, by the use of a small amount of gum tragacanth, and into these, platinum wires about three inches long were inserted. These pieces were again fired to a high temperature. The specimens were then ground on one side to a smooth surface so as to form a good contact. Such small plates were similarly prepared from Georgia kaolin.

In carrying out the experiment proper, two specimens of different compositions were placed one on top of the other in an electric furnace, the platinum wires being connected with a millivoltmeter by means of a long wire of the same metal. The

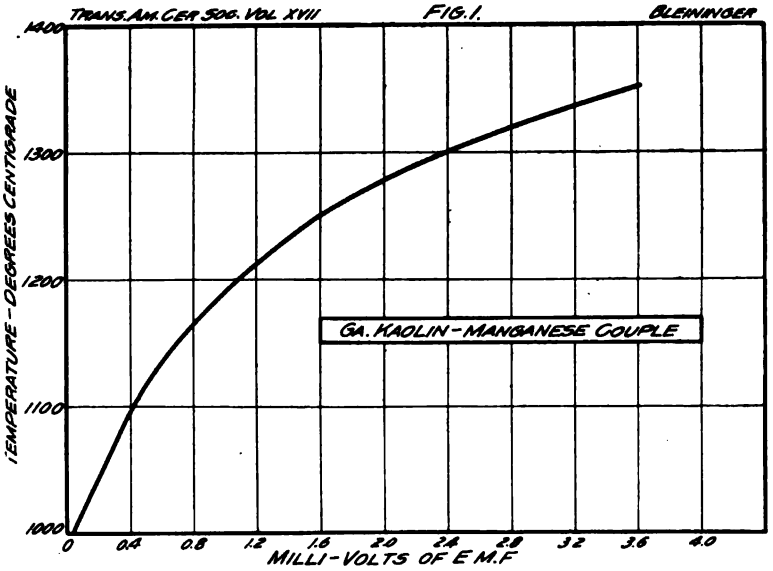
[1] By permission of the Director, Bureau of Standards.

TABLE I—DIFFERENCES IN POTENTIAL

COMBINATION	MILLIVOLTS, AT THE TEMPERATURES (DEGREES C.)											
	850°	900°	950°	1000°	1050°	1100°	1150°	1200°	1250°	1300°	1350°	
$ZnO.2\,SiO_2$+ ... $MnO\ .2\,SiO_2$— ..	....	0.05	0.07	0.09	0.12	0.15	0.23	0.29	0.31	0.60	0.65—	0.80
$ZnO.2\,SiO_2$+ ... $CuO.2\,SiO_2$— ...	0.05	0.10	0.15	0.20	0.30	0.35— 0.40	0.60	0.85— 1.00	0.90— 1.10	0.90— 1.10	1.50— 1.65	....
$ZnO.2\,SiO_2$+ ... $FeO.2\,SiO_2$— ...	0.02	0.05	0.10	0.15— 0.20	0.32	0.40	0.50— 0.60	0.70	....	....	....	....
Ga. Kaolin+ .... $FeO.2\,SiO_2$— ...	0.05	0.15	0.21	0.33	0.52	0.75	1.05	1.40	....	....	....	....
Ga. Kaolin+ .... $ZnO.2\,SiO_2$— ...	....	0.02	0.05	0.08	0.15	0.35	0.55	0.90	1.70	....	....	....
Ga. Kaolin+ .... $MnO.2\,SiO_2$— ..	....	....	0.05	0.25	0.35	0.70	1.10	1.60	2.40	3.60	....	....

furnace was heated by means of a platinum coil, using an alternating current. A thermocouple was employed for the determination of the temperature. Differences in potential were indicated in each case. These readings are compiled in Table I.

From these results, it is evident that increasing potentials are shown with rise in temperature as was to be expected from the fundamental considerations. Figure 1 shows graphically the E. M. F. temperature relation for the kaolin—$MnO.2\,SiO_2$ combination.



In promised to be of interest also to determine whether any polarization effect could be detected. This was tried out by conducting a direct current through the piece and upon breaking connection noting the deflection of the millivoltmeter. It was found that polarization was invariably present. The deflection was found to be the greater, the greater the potential observed in the first set of experiments and the higher the furnace temperature. This furnishes additional evidence towards the as-

sumption that silicates at higher temperatures are partially ionized. These phenomena are evidently also connected with the diffusion taking place between one silicate and another.

The writer desires to acknowledge his indebtedness to Mr. C. S. Kinnison for preparing the specimens and making the necessary readings.

DISCUSSION

Mr. Hice: I would like to ask Mr. Bleininger, what the effect of repeated heatings is upon the current generated?

Mr. Bleininger: So far, we have not been able to detect any difference.

THE TECHNICAL CONTROL OF A WINDOW-GLASS TANK FURNACE

BY C. J. BROCKBANK

Until a few years ago, the history of sheet and plate glass manufacture in this country was largely a story of failure, exasperating and protracted manufacturing difficulties, and unprofitable operation. Technical methods and technical men were alike looked upon with suspicion, an attitude largely encouraged and fostered by the glass-makers of the old school. This attitude has now almost entirely disappeared, due to the remarkable success of a few companies adequately equipped to attack their difficulties by scientific methods.

It is difficult to conceive of an industrial process more in need of technical control than the operation of a large glass tank. These difficulties have been evaded by the operation of pot furnaces, in preference to tank furnaces, so that in case of trouble the losses are not so serious. The use of pot furnaces greatly increases the cost of production, without, in the majority of cases, yielding a product any better in quality than can be obtained in a large tank, the operations of which are standardized and carefully and unremittingly controlled.

The subject may be subdivided for convenience as follows:

1. The construction of tank.
2. Materials used in construction.
3. Composition of glass mixture (or "frit"), and consideration of ingredients of mixture.
4. Operation of gas producers.
5. Temperature of control and pyrometry.
6. Determination of composition, and origin of defects in the glass. The adjustment of mixture, temperature of tank and other conditions to remedy these defects.

THE CONSTRUCTION OF TANK

The actual design of the tank will vary in each factory, and considerable variations may be made in proportions without

affecting greatly the efficiency of operation. Attention may be directed, however, to the following points which are of extreme importance:

The width of the tank must be sharply constricted towards the working end of the same, at about the position occupied by the floats. This tank design gives a glass more free from the ordinary defects, which are chiefly particles of undissolved "frit."

Projecting ledges and corners in the fire clay blocks composing the lining should be carefully avoided. Below the level of the "metal," such corners are more rapidly weathered and disintegrated than the rest of the surface, and give rise to clay stones in the finished product; above the metal, they are fused down very rapidly by the hot furnace gases and alkali vapors, and drop into the glass causing the defect known as "furnace drops."

The crown of the furnace should not be more than 6 to 8 feet above the level of the metal. Many high crowned tanks have been built in accordance with the "free flame" theory, but they have been found uneconomical. The theories of the free flame and radiation are in themselves correct, but their failure in practice is due to the fact that the gas and air do not mix thoroughly unless baffled, and the full heat of the fuel is not developed. In a high crown furnace, the gas issuing from the port always has a tendency to float to the top of the crown, although this tendency can be counteracted, to some extent, by arranging the gas ports below the air ports.

MATERIALS USED IN CONSTRUCTION

In the selection of materials used in the construction of a glass-tank, we are governed mainly by the following considerations: refractoriness, power to resist sudden changes of temperature, and, in the case of tank blocks, the property of uniform solubility. The latter point has not received anything like the attention it deserves, for it is obvious that, if in the manufacture of a tank block, a hard burnt refractory *chamotte* is bonded with virgin clay of the same refractoriness as the *chamotte,* the

degree of solubility of the constituents will differ. The clay bond will more readily dissolve than the particles of grog, which will float off and give rise to clay stones in the product. By using a highly refractory clay bond, we may avoid this trouble, but the point to be emphasized is the danger of using a very refractory grog with a comparatively fusible cementing material. The clays of Grossalmerode are largely used in Germany for this purpose, because they possess in a high degree this property of uniform solubility, but they dissolve so readily in the glass that the life of the tank is considerably shortened.

Acid materials, *i. e.*, those containing sand or free silica, give much greater satisfaction than one would believe on theoretical grounds. The physical state of the ingredients of the clay is a very important factor in determining the degree of solubility in the glass, and, as a matter of fact, tank blocks have been used containing a considerable quantity of admixed sand with satisfactory results.

Dimensions of Blocks. The durability of a tank block is largely influenced by its thickness, for the thickness, within certain limits, governs the temperature of the face in contact with the glass. A thick block will keep its inner face hotter and dissolve more rapidly than a thinner one of the same material. Because of this fact, it is desirable to make the blocks as thin as mechanical considerations permit, where the chemical action is greatest. If this is done devitrification is not at all to be feared through excessive cooling. In the writer's experience, even when the blocks have worn very thin, and in cases where they had to be cooled with water, there were no signs of devitrification. This is partially to be explained by the higher alumina content of the glass near the blocks, the presence of alumina lessening the tendency to devitrification in crown glasses, as explained in a recent paper in these transactions.[1]

The nature of the glass melted in a tank will naturally affect the life of the tank blocks. The action of the free sodium sulphate ("salts") is well known. A glass comparatively free from alumina will attack the blocks much more rapidly than

[1] Vol. XV, page 600. An Investigation of the Surface Devitrification of Glasses under Thermal After-treatment.—C. J. Brockbank.

one in which this ingredient is present in small amounts, say one or two percent. Consequently the introduction of alumina in some form is desirable from this point of view. This can be effected by the use of a sand containing a high alumina content, or by the use of other materials such as felspar, as in done in Germany.

COMPOSITION OF GLASS MIXTURE

The mixture will be varied, within narrow limits, from time to time as required by the quality of the finished product. The following mixtures are given as standards, both yielding excellent glass, over a long period of time.

	No. 1	No. 2
	Parts per 1000	
Sand	557	548
Limestone	171	165
Salt cake	230	263
Soda ash	25	4
Coal	14	17
Arsenic (As_2O_3)	2	2
Pyrolusite (MnO_2)	1	1
	1000	1000

It will be noticed that in mixture No. 2 the greater part of the soda ash has been replaced by salt cake. This makes a cheaper mixture and appears to yield a glass fully equal in quality to No. 1. It is, however, necessary to maintain a closer balance in the ratio salt-cake to coal than is necessary with mixture No. 1. The color of the glass is generally a pure blue, and it may be readily distinguished from that made from the soda-ash mixture, which is a yellowish blue, and not so brilliant in appearance. In this connection it may be mentioned that the blue color of glasses made from a salt-cake mixture is not altogether due to the iron present as an impurity, but is due to the formation of compounds of sulphur and alumina analogous in composition to ultramarine.

The sulphur dioxide evolved from sulphate mixtures always produces this blue color, which is quite characteristic, and can be distinguished from the blue color due to iron only, by measuring the absorption curve of the light transmitted by it.

The chemical reactions taking place during the fusing of glass mixtures of this type, are particularly complex. It was formerly thought that the reduction of the salt-cake by carbon could be expressed by a combination of the following equations:

$$\text{I.} \begin{cases} Na_2SO_4+4\,C=Na_2\,S+4\,CO. \\ Na_2S+Na_2SO_4+2\,SiO_2=2\,Na_2SiO_3+SO_2+S. \end{cases}$$

$$\text{II.} \begin{cases} \text{(a)}\ Na_2\,SO_4+SiO_2+C=Na_2\,SiO_3+CO+SO_2. \\ \text{(b)}\ Na_2SO_4+SiO_2+3\,C=Na_2\,SiO_3+3\,CO+S. \end{cases}$$

The first set of equations require four molecular weights of carbon for the reduction of two molecular weights of sodium sulphate, or 142 pounds of sodium sulphate require 24 pounds of carbon. Salt-cake contains approximately 96 percent of $Na_2\,SO_4$, so that mixture No. 2 using 263 pounds of salt-cake would require theoretically 42.6 pounds of carbon for reduction.

In the second set of equations, the quantity of carbon required depends on the proportion of sulphurous acid to sulphur evolved by the mixture. If sulphurous acid alone be evolved, the carbon consumed would be 21 pounds. If sulphur only be evolved, then 64 pounds of carbon are required. Neither of these limits would ever be reached, and it is much more probable that the reactions expressed in the first case are more nearly correct. The carbon required in practice is so different to that required on theoretical grounds, that we are forced to the conclusion that other reactions of an obscure nature, in which the lime probably plays an important part, must take place.

INGREDIENTS OF MIXTURE

1. **Sand.** Sand, constituting the greater proportion of the mixture, represents about 72 percent of silica of the total of glass-forming oxides as calculated from the composition of the frit. Actual analyses of the resulting product always show less SiO_2, and this is partly due to the presence of moisture and

organic matter in the sand. The silica contents of a window-glass should not fall below 70 percent, the upper limit lies between 74-75 percent. Above this amount, the glass becomes too hard and infusible. Sand being by far the cheapest ingredient, and generally very pure, it is economical to use as high an amount as is possible without unduly increasing the cost of melting. The color will also be favorably influenced by this.

The percentage of iron present as impurity should not exceed 0.3 percent. The alumina may be very high, and as previously noted, high alumina is a positive advantage.

2. **Lime.** The lime contents of a tank glass should not exceed 13 percent, and are preferably kept below 12½ percent, as high lime renders the glass hard and brittle, and produces a tendency to devitrification. On the other hand, the quality of the glass when made is superior when the lime is high, being physically and chemically more resistant, easier to clean, more brilliant, and color-permanent. As indicated previously, the lime plays an important part in the reduction of the salt-cake during melting, so that a decrease in limestone must always be compensated for, by an increase of coal in the mixture. The proportion varies with the furnace and other conditions, but is approximately of the order of ¼ pound of coal added for 3 pounds of limestone removed and *vice-versa.*

3. **Salt-cake.** The percentage of sodium oxide in the glass, should not fall below 12 percent, unless lime is below 12 percent and silica above 72 percent. Soda contents of 15 percent have been used, but 14 percent should be regarded as the upper limit. The soda is derived partly from the salt-cake and partly from soda-ash. The proportion of salt-cake that can be used depends upon the furnace, the character of the flame, and also upon the proportion of lime and silica present. The sodium sulphate is the cause of a good many of the troubles experienced in the manufacture of tank-glasses. Both sodium sulphate and sulphide are soluble in glass, and apt to be thrown out of solution in the cooler parts of the furnace, the sulphate as stones and the sulphite as greenish yellow bubbles, commonly called *blibe.*

These troubles are sometimes very obstinate and cannot al-

ways be corrected by varying the relative amounts of salt-cake and coal, since the total soda content cannot be reduced without hardening the glass, which in time necessitates altering the proportions of silica and lime. It must be noted that the alkali contents of a glass cannot be calculated from the composition of the mixture, as there is considerable loss of Na_2O due to volatilization and incomplete decomposition, and also due to the cullet constantly being re-introduced. This loss of alkali varies but will usually be between 0.5 and 1.5 percent.

4. **Coal.** The proportion of coal required depends greatly on the nature of the flame in the furnaces, and the proportions of sand and limestone present. Insufficient coal causes the formation of "salts," or allows undecomposed sulphate to remain in the glass. Excess of coal causes the glass to show *blibe* and color from the formation and subsequent expulsion of sodium sulphate. The color is also influenced by coal in excess, a moderate excess giving a brown to green coloration. It is, however, worthy of note that a further increase of coal causes this color to disappear, and the glass becomes white.

5. **Arsenic.** This material is used almost universally in tank-glass mixtures, but it is very doubtful if it has any beneficial effect. It does, on the other hand, contribute to make the color unstable in sunlight. The action of arsenic in glass mixtures depends upon the following properties:

(a) Arsenious oxide (As_2O_3)—the form in which arsenic is always used in a glass mixture—is completely volatile at 200° C. At a higher temperature, its vapour undergoes dissociation and expands very considerably.

(b) When used in a glass mixture containing nitrates or other oxidizing materials, arsenious acid is readily converted into arsenic acid. This substance is much less volatile and remains partly dissolved in the glass, or may even appear as a crystalline compound on the surface of the molten glass, this defect being quite common.

(c) Under reducing conditions, such as obtain in the fusing of a sulphate mixture, arsenious acid readily releases its oxygen to any carbon and sulphur that may be present, and is

reduced to the condition of metallic arsenic, which is quite as volatile as the lower oxide and consequently escapes. The action of arsenic in a glass melting, therefore, is partly chemical and partly mechanical, its mechanical function being the production of a good open "boil" in the glass, and the consequent elimination of small air bubbles. It is very unlikely that any appreciable mechanical or chemical effect can be exerted by arsenic in a mixture containing coal, and its retention in such mixtures is largely a matter of superstition, and false inferences drawn from its positive action in oxidizing mixtures.

6. **Manganese.** (MnO_2). This material is used as a decolorizer so called. Actually it masks the blue color due to iron and sulphur compounds by the complementary pink color produced. Complete neutralization of the blue color should never be attempted, or the result will be a serious loss of brilliancy in the product, and the danger of variations in furnace conditions causing the pink color to appear in excess.

7. **Cullet.** If, as is nearly always the case, a difference exists between the composition of the glass—resulting from the melting of the raw mixture alone—and the composition of the cullet, the proportion of cullet used will greatly influence the composition of the glass produced. It is not, however, true that the losses of Na_2O in the furnace will **continuously** alter the composition of the glass. If the composition of the raw mixture, proportion of cullet, and furnace conditions remain approximately constant, the composition of the glass must soon attain constancy also. This is proved mathematically in this paper.

OPERATION OF GAS PRODUCERS

The gas producers feeding a tank-furnace require unremitting attention, and they should be controlled by the frequent analyses of the fuel used and the gas produced. They are usually worked on the cold principle, that is to say, looking on the fuel bed from the poke holes on the top, the bed looks black, or a deep cherry red color, and it must be kept in this state by frequent poking. The hand labor required to maintain this condition is very much reduced in the new producers having a re-

volving hearth. The quantity of steam injected is adjusted so that the hydrogen in the gas does not exceed 20 percent, otherwise the flame will be too keen and short. What is needed in a furnace of this type is a large volume of gas of a moderately rich character, rather than a smaller volume of high calorific value.

A typical analysis of a satisfactory producer gas follows:

	Percent
Carbon dioxide	4-6
Oxygen	nil
Carbon monoxide	18-20
Hydrogen	12-16
Marsh gas (CH_4)	4- 5

Washing the gas has been attempted in order to minimize the risk of smoke streaks on the surface of the molten glass but without success, because of the loss in heating efficiency, due to the admission of cold gas into the regenerators.

TEMPERATURE CONTROL AND PYROMETRY

The proper control of the temperature of a glass tank is of the highest importance, particularly at the working end. If the temperature be too high, the glass will be too fluid to gather successfully, and if too low the glass will be too viscous and will be likely to entrain air bubbles during the gathering operation. The temperature at which the right degree of viscosity is obtained will vary with the composition of the glass, the alumina having a profound influence. With glasses of the composition indicated previously, a temperature of 1190°C will be found approximately correct for the working end of the tank. At the melting end, the temperature may vary from 1290°-1350°. It is desirable to keep this as constant as possible by feeding on small amounts of frit frequently. Feeding on large quantities of frit at infrequent intervals greatly reduces the temperature of the glass already melted, and is liable to cause devitrification.

After using almost every type of pyrometer on the market, the writer prefers the Wanner type for use at the melting end, and a Fery recording pyrometer for the working end of the

tank, the latter being sighted directly on the floats through an orifice in the brickwork at the side. Thermo-couples probably give slightly more accurate readings, and respond more readily to sudden changes of temperature, but their life is extremely short owing to the sulphur gases, which penetrate any kind of protective tube and make the platinum wire brittle.

DETERMINATION OF COMPOSITION AND ORIGIN OF DEFECTS IN THE GLASS

The defects commonly occurring in window glass are of the following nature:

(1) "Salts"—due to incomplete reduction of salt-cake.
(2) "Sulphate" stones—due to the same cause as (1), but formed by the recrystallization of sodium sulphate that has dissolved in the glass.
(3) "Dim blibe"—a dark color generally first seen as a smoky film on the surface of the glass.
(4) Clay stones—formed usually by the disintegration of the tank blocks, but also a result of gathering too close to the floats.
(5) Furnace drops—caused by fused clay dropping from the crown of the furnace.
(6) Devitrification stones.
(7) Striae and wreath.
(8) Hardness and brittleness.

The first three defects commonly arise from some change in the character of the flame gases; and a change in the coal, salt-cake ratio and possibly in the limestone, salt-cake ratio becomes necessary. The daily determination of the amount of free sodium sulphate in a tank-glass often enables one to anticipate trouble of the above nature. When analyses show more than one percent of free Na_2SO_4, stones may be expected. A method for determining the free sulphate in tank-glasses is given in a previous volume of the Transactions. The cause of clay stones has been previously discussed. Very little can be done when these appear. They can be avoided by the use of good tank blocks of uniform solubility. Devitrification stones when small can be

remedied by increasing the temperature of the tank for a few hours, by protecting it from cold draughts and also by adding alumina in some form as indicated under section three. Striae and "wreath" result mainly from change of mixture, but the solution of fire clay in glass, due to either bad clay or excessive local heating, may also produce it.

The causes of hardening in glass are very obscure; hardening accompanied by an increase in the lime contents in the glass appears to go on more or less continuously in all tank-furnaces. This defect is generally met by a reduction in the limestone.

All stones, or solid defects, should be examined with a petrological microscope when their nature can be readily determined. If they are large enough to extract from the glass, an analysis is sometimes desirable. Typical analysis of two of the above defects are here given:

Devitrification Stones

	Percent
SiO_2	78.19
CaO	4.48
$Fe_2O_3+Al_2O_3$	1.15
Na_2O	15.66
	99.48

Furnace Drops

	Percent
SiO_2	57.91
CaO	5.78
Fe_2O_3	1.04
Al_2O_3	19.17
Na_2O	15.69
	99.59

EFFECT OF COMPOSITION OF CULLET

Let the contents of one constituent of the glass calculated from the composition of frit be $=K$ per ton of glass. Let the contents of one constituent of the cullet, as found by analysis

at one particular stage be=l per ton of glass. Let A tons of frit be used with B tons of cullet; A tons of frit make A' tons of glass. Let m be the loss of the constituent above referred to, when glass made from frit alone is compared with the frit as calculated; then the glass made from A tons of frit contains

$$A'\,(K-m) \text{ of that constituent.}$$

Let n be the loss of the constituent suffered by a ton of cullet in passing once through the furnace; then the glass from B tons of cullet contains $B\,(l-n)$ of the constituent, or of the entire glass leaving the furnace. $A'+B$ tons contain:

$$A'(K-m)+B(l-n) \text{ of that constituent.}$$

One ton contains $\dfrac{A'}{A+B}(K-m)+\dfrac{B}{A+B}(l-n)$ of that constituent. But this is now the composition of the new cullet, when it re-enters the furnace with more frit of the original composition, calling l_1 the composition of the cullet after passing once through the furnace. $l_1=\dfrac{A'}{A'+B}(K-m)\dfrac{B}{A'+B}(l-n)$.

The same argument now applies using l_1 in place of l; and the composition on next leaving the furnace—assuming only that the conditions within the furnace have remained the same—will be

$$l_2=\frac{A'}{A'+B}(K-m)+\frac{B}{A'+B}(l_1-n)$$

$$l_2=\frac{A'}{A'+B}(K-m)\frac{B}{A'+B}\left[\frac{A'}{A'+B}(K-m)\frac{B}{A'+B}(l-n)-n\right]$$

$$l_2=\frac{A'}{A'+B}(K-m)\frac{A'B}{(A'+B)^2}(K-m)+\frac{B^2}{(A'+B)^2}(l-n)-\frac{B}{A'+B}.n$$

Similarly, after another round the composition will be

$$l_3=\frac{A'}{A'+B}(K-m)+\frac{B}{A'+B}(l_2-n)$$

$$=\frac{A'}{A'+B}(K-m)\frac{B}{A'+B}\left[\frac{A'}{A'+B}(K-m)\frac{A'B}{(A'+B)^2}\right.$$

$$\left.(K-m)+\frac{B^2}{(A'+B)^2}(l-n)\frac{B}{A'+B}.n\right]$$

$$=\left(\frac{A'}{A'+B}+\frac{BA'}{(A'+B)^2}+\frac{A'B^2}{(A'+B)^2}\right)(K-m)+$$

$$\frac{B^2}{(A'+B)^3}(l-n)-\frac{B^2}{(A'+B)^2}.n$$

Consequently, after n rounds, the composition will be

$$l_n=\left(\frac{A'}{A'+B}+\frac{A'^nB}{(A'+B)^2}+\ldots\ldots+\frac{A'^nB^n}{(A'+B)^2}\right)(K-m)$$

$$+\frac{B^n}{(A'+B)^n}(l-n)-\frac{B^{n-1}}{(A'+B)^{n-1}}.n$$

$$=\frac{A'}{A'+B}(K-m)\left\{l+\frac{B}{A'+B}+\frac{B^2}{(A'+B)^2}+\ldots\ldots+\right.$$

$$\left.\frac{B^n}{(A'+B)^n}\right\}\textit{et cetera.}$$

Assuming for the sake of illustration, that $A'=2$ and $B=1$

$$A'+B=3$$

$$\text{then}\frac{A'}{A'+B}=0.66 \text{ while}\frac{B}{A'+B}=0.33$$

$$\left(\frac{A'}{A'+B}\right)^2=0.44 \qquad \left(\frac{B}{A'+B}\right)^2=0.11$$

$$\left(\frac{A'}{A'+B}\right)^3=0.14 \qquad \left(\frac{B}{A'+B}\right)^3=.036$$

With increasing indices therefore, these terms rapidly become negligibly small, so that ultimately the first term of the above expression for l_n becomes of a constant value, while the other two terms disappear. It follows that, after four or five rounds, the glass, under the conditions assumed will attain a constant composition which will not be the same as that calculated from the frit, but will bear a constant ratio to it.

VARIATION IN SODA, LIME, AND MAGNESIA CONTENT OF A GLASS OF THE TYPE RO $3\,SiO_2$[1]

BY C. C. RAND

The object of the investigation is to determine the effect of varying the soda, lime, and magnesia in a glass of the type $RO.3\,SiO_2$. The glasses studied are those comprised in the triaxial group (Fig. 1) with $MgO.3\,SiO_2$, $CaO.3\,SiO_2$, and $Na_2O.3\,SiO_2$ as the apices of the triangle, the increment being 1/15 equivalent RO.

The materials used were flint, precipitated magnesium carbonate, whiting and soda ash. A batch of about 500 grams was ground in a porcelain ball mill for four hours, then introduced into the crucible, previously heated to about 1000°C. in a small gas and compressed air pot furnace. The temperature was raised until the melt was practically free from bubbles, then the contents of the crucible were poured on to an iron slab and rolled into a sheet approximately one-eighth inch thick.

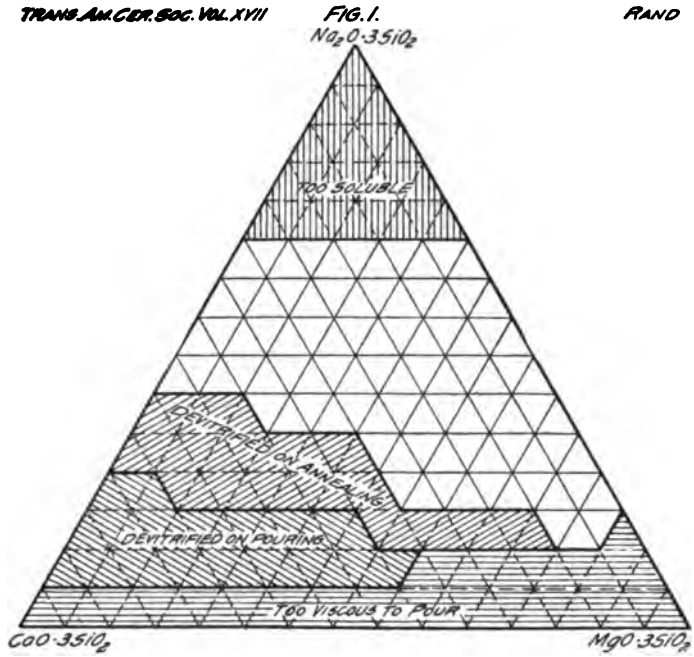
The three limiting factors will be excessive solubility, too great a tendency to devitrify, and high viscosity.

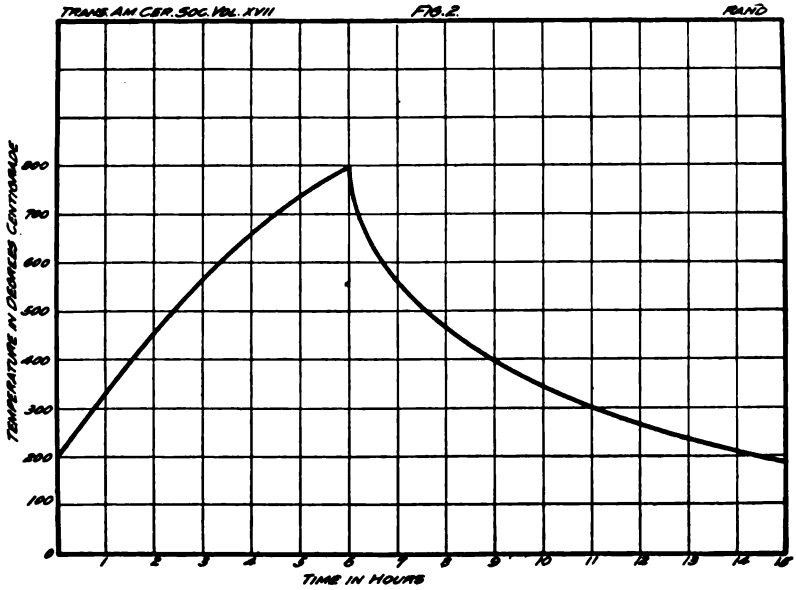
The work on solubility has not been carried out sufficiently to be presented, but the glasses containing above .66 equivalent Na_2O have not been considered, since they will be concerned in neither the devitrification nor viscosity limits.

The only viscosity limit which has been established so far is that set up roughly by the glasses in the lower shaded portion (Fig. 1). These could not be obtained in a sufficiently fluid condition to permit of their being poured and rolled.

In establishing the limits due to tendency to devitrify, surface devitrification has been neglected, since the annealing was carried on under conditions which caused all the glasses considered to suffer devitrification to some extent. Therefore, only those glasses which became opalescent or practically opaque have been regarded as devitrified.

[1] By permission of the Director, Bureau of Standards.


TRANS. AM. CER. SOC. VOL. XVII
FIG. 1.
RAND
$Na_2O \cdot 3SiO_2$
TOO SOLUBLE
DEVITRIFIED ON ANNEALING
DEVITRIFIED ON POURING
TOO VISCOUS TO POUR
$CaO \cdot 3SiO_2$
$MgO \cdot 3SiO_2$


TRANS. AM. CER. SOC. VOL. XVII
FIG. 2.
RAND
TEMPERATURE IN DEGREES CENTIGRADE
800
700
600
500
400
300
200
100
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
TIME IN HOURS

The middle shaded portion (Fig. 1) contains those glasses which became opalescent or opaque upon pouring and rolling.

The upper shaded portion contains those glasses which devitrified on annealing according to the time-temperature curve shown in Fig. 2. The samples were placed upon small stilts in a gas muffle, and it was found that a temperature of 800°C. was necessary to cause all the glasses to deform, and at this temperature the deformation of the extremely high MgO glasses was very slight. It will be noticed that this form of annealing will encourage devitrification, since we know that by reheating a glass, conditions favorable to crystallization are set up, the point of greatest tendency to crystallize being reached before the point of highest velocity of crystallization. This, together with the comparatively high temperature to which they were subjected, probably accounts for the surface devitrification of the normal glasses.

Since the annealing was not carried on under commercial conditions, and since surface devitrification was not considered, the limit established here has no direct practical significance. It merely shows that as we replace CaO by MgO the amount of devitrification is decreased when the glasses are subjected to the same annealing treatment. Whether this difference is due principally to differences in viscosity or to greater or less tendencies to crystallize cannot be determined until each glass has been annealed over a separate temperature range. However, Brockbank[2] has shown that by replacing lime by magnesia the tendency to surface devitrification was decreased, while the softening point remained the same. Furthermore, the decrease in devitrification upon pouring and rolling which is caused by replacing CaO by MgO, seems to indicate that a high MgO glass has a lower velocity of crystallization than a high CaO glass, since in the low viscosity necessary for pouring and rolling, its effect on devitrification would be much less than in annealing.

Both in the glasses which devitrified on pouring and those which devitrified on annealing, a marked decrease in the amount of crystallization accompanies an increase of MgO at the expense

[2] *Trans. Amer. Cer. Soc.*, Vol. XV, p. 600.

of CaO. The high CaO end of the upper boundary has a ratio of Na_2O to CaO of 2:3, while the high MgO end has a ratio of Na_2O to (CaO+MgO) of 2:13.

It will be seen from Figure 1 that the limit established by high MgO will probably be due, not to devitrification, but to high viscosity. In no case did devitrification occur in a glass containing no CaO.

By determining the solubility, devitrification and viscosity limits effective under industrial conditions, it is hoped that some ideas will be gained as to the practical value of dolomitic limestones.

THE PRODUCTION, MANUFACTURE AND USE OF COMPOUNDS OF BARIUM

BY WARREN E. EMLEY AND S. ECCLES YOUNG[1]

The amount of barium salts annually used in the United States is rather small as expressed in dollars and cents, but they find their way into so many industries that they have become commercially quite important. Thus, the sulphate is used in the manufacture of paint, paper, rubber, leather, and textiles; the peroxide for making oxygen; and the carbonate and chloride are valuable reagents to prevent the efflorescence on brick. The natural growth of this last use seems to have been hampered somewhat by the fact that very little barium carbonate is produced in this country, though a considerable quantity of barium sulphate is mined. From 1912 to 1913, the importations of natural carbonate decreased from $15,000 to $13,000,[2] while those of the artificial carbonate increased from $10,000 to $39,000. Inasmuch as this artificial carbonate is made from the sulphate, it is thought that perhaps a resume of the facts of the case might stimulate such an industry in this country.

Barium belongs to the group of alkaline earth metals which includes calcium, magnesium, and strontium. There is reason to believe that barium is as widely distributed as calcium or magnesium, but in such small quantities that it is not generally reported in the ordinary chemical analysis. The analyses of a large number of rocks lead to the conclusion that barium ranks about thirteenth in the order of abundance of the elements, and the entire lithosphere contains about one-tenth of one percent of barium oxide.[3] Under the action of weathering these rocks disintegrate, and their components are frequently dissolved and transported by water. If conditions are favorable, the calcium or magnesium may become concentrated and precipitated in the form of carbonates, as limestone, chalk, dolomite, magnesite; or in the form of sulphate, as gypsum. Similarly, barium may be

[1] By permission of the Director, Bureau of Standards.
[2] Jas. M. Hill—Production of Barytes in 1913—U. S. Geol. Sur.
[3] F. W. Clark—*Data of Geochemistry, U. S. Geol. Sur., Bull.* 330 (1908).

deposited as the carbonate (witherite) or as the sulphate (barytes). There is evidence to show that, in some localities at least, the barium has been brought up from below by subterranean waters, instead of being concentrated by surficial disintegration.[4]

There are then two minerals which serve as commercial sources of barium—the carbonate, witherite, and the sulphate, barytes. Witherite is much more valuable on account of the facility with which it can be transformed into other salts, but unfortunately no workable deposits of witherite are known to occur in the United States. Our entire domestic supply is derived from barytes.

Barytes generally occurs in small veins, lenses, or even mere fragments, imbedded in a matrix of sandstone, limestone, or clay, and in such a condition that it is usually necessary to hand-pick it in order to obtain it reasonably free from the surrounding impurities. This mode of occurrence is probably the main drawback to the industry, for it would hardly pay to use any but the crudest methods of mining when the deposits are so small individually, and so uncertain. Thus we find that in Missouri (the chief producing area of the United States) "practically all the barytes is mined from shallow shafts and open cuts by farmers or other people during periods of inactivity in other industries.[5] Besides the Missouri district, the only producing area in the United States is in the southern Appalachian region, embracing small deposits in Virginia, Tennessee, North Carolina, South Carolina and Georgia. Abandoned barytes mines may be found in Connecticut, Kentucky, Nevada, New York and Pennsylvania, and deposits have been observed in almost every State in the Union.[6] The total production of domestic crude barytes in 1913 was valued at $156,275, at an average price of $3.45 per ton, hand-picked, cobbed, and sorted at the mine. In addition to this, there was imported $61,409 of crude barytes, under a duty of 15 percent *ad valorem*.

[4] A. A. Steel—*Geology, Mining, and Preparation of Barite in Washington Co., Mo., Bull.* 88, *A. I. Min. E.* (1910).
[5] Hill—*loc. cit.*
[6] Samuel Sanford and R. W. Stone—*Useful Minerals of the U. S.; U. S. Geol. Sur., Bull. No.* 585, 1914.

Crude barytes is a white, opaque or translucent mineral, generally made up of aggregates of straight or slightly curved plates, although it sometimes occurs in granular or fibrous masses. It is frequently quite pure, the chief impurities being grains of foreign matter, such as galena or pyrites, disseminated throughout the mass, or stains of iron or clay which discolor the surface. Besides being a source of other barium salts, it is used as such in a number of industries, because it possesses three distinctive properties: It is white in color, is extremely heavy, and is not attacked to any extent by any ordinary reagent. In order to prepare the crude material for the market, it is necessary merely to free it from its impurities, and grind it to the desired size. The usual mode of refining is to break the crude material to a size ranging from one-eighth inch to one-half inch, depending on the amount of iron present. The gross impurities can be mostly removed by jigging. The discoloring stains on the surface of the lumps are bleached out with sulphuric acid. The barytes is treated with acid having a density of about 20° to 30° Beaume, and the mix is stirred with live steam until bleaching is complete. This takes from 6 to 80 hours, depending upon the quality of the raw material. The barytes is then dried and ground to an impalpable powder, when it is ready for the market as refined barytes.[7] A more efficient method is to grind the ore before bleaching instead of afterwards. If the discoloring stains are very persistent, it is sometimes necessary to roast the ground ore with a mixture of sodium chloride, sodium nitrate, and sulphuric acid. This converts the iron and manganese to the chlorides, which can be readily removed by subsequent bleaching. Another commercial grade of barium sulphate is a manufactured, rather than a refined, article, and is known to the trade as *"blanc fixe."* The process of manufacture is essentially the same for *blanc fixe* as for all other barium salts. Crude barytes is finely ground and mixed with one-fourth of its weight of powdered coal. The mix is burned in a rotary kiln, and the clinker produced contains 65 to 68 percent barium sulphide, the

[7] Edwin Higgins, Jr.—Barytes and its Preparation for the Market.—*Eng. News*, Vol. 53, p. 196 (1905).

balance being mainly barium carbonate.[8] This barium sulphide can be dissolved in water, purified and treated with various reagents to produce different barium salts. To make *blanc fixe,* the reagent is, of course, sulphuric acid, which precipitates the insoluble barium sulphate in a form which is purer, more finely divided, and more nearly white than can ordinarily be produced by a mere refining process.

Refined barytes or *blanc fixe* is used as a filler or adulterant in the manufacture of paper, rubber, leather, and textiles. Since these materials are generally sold by the pound, the high specific gravity of barium sulphate renders its use quite attractive to the manufacturers. Its white color enables its presence to be readily concealed, and its extreme insolubility makes it permanent.

The use of barytes to replace white lead or zinc white in the manufacture of paint was formerly considered an adulteration. While it is probably true that the quality of paint produced from it is inferior for use on either wood[9] or steel,[10] barytes has achieved recognition as a true white pigment rather than an adulterant.[11]

In the paint and rubber industries, a mixture of barium sulphate and zinc sulphide is being marketed under the name of "lithophone." Barium sulphide, prepared by reduction of the sulphate with coal as described above, is dissolved and treated with a solution of zinc sulphate. The resultant precipitate of barium sulphate and zinc sulphide is calcined at a high temperature, thrown into water, and pulverized.[12] When used as a paint, lithophone is claimed to have a greater covering capacity than barytes. If lithophone is added to rubber, the resultant product can be made harder and tougher, with increased resistance to cutting and abrasion.[13] In either industry lithophone cannot be considered as a filler or adulterant.

The production of refined barytes in the United States dur-

[8] Edward K. Judd,—Barytes Industry of the South—*Eng. and Min. Jour.*, 1907, p. 751.
[9] Inspection of White Paint Test Fence at Washington, D. C. *Com. D-1, A. S. T. M.*, 1914.
[10] Inspection of Steel Plates at Atlantic City.—*Com. D-1, A. S. T. M.*, 1914.
[11] Analyses of White Pigments—*Com. D-1, A. S. T. M.*, 1914.
[12] *U. S. Geol. Surv.—Min. Res. for 1911*, part 2, p. 968.
[13] Philip Schidrowitz—*Rubber*, p. 189.

ing 1913 was valued at $525,300. $35,840 worth of refined barytes and $62,785 worth of *blanc fixe* were imported, under a duty of 20 percent *ad valorem*. It will be noted that the refined barytes sold at an average price of $14.18 per ton, as compared with $3.45 for the crude material.

Next to the sulphate, the most important salt of barium is the peroxide or binoxide, as it is known to the trade. This material can be produced from the sulphate by the following general method: The mixture of sulphide and carbonate obtained by the reduction process described above is treated with carbon dioxide until all of the barium is precipitated as the insoluble carbonate. This is mixed with coal and a little lime or magnesia, and is heated in retorts to 1200°C., when the carbonate is reduced by the coal. The mass is cooled in a stream of pure dry air.[14] The resultant barium peroxide is a dark gray powder, which possesses the valuable property of being able to give up half its oxygen when heated to about 800°C., and reabsorbing it if permitted to cool in air. It is therefore used to extract oxygen from the air. Theoretically, the amount of oxygen which can be extracted by a given weight of peroxide by repeated heating and cooling is unlimited, but practically, the pure peroxide soon loses its efficiency This is due to incipient fusion of the material, so that less surface is presented for the absorption of oxygen. It is on this account that the small amount of lime is added; to prevent fusion and keep the mass porous. The same end may be accomplished by heating the pure peroxide in a partial vacuum, when the oxygen is liberated at a lower temperature and with less danger of fusion.

In 1913, the imports of barium peroxide were valued at $239,000, under a duty of one and one-half cents per pound. The amount of this material used has been gradually decreasing, probably because of the competition of liquid air as a source of oxygen.

Among the other salts of barium, the only ones of particular commercial importance are the carbonate and the chloride. These can be made from the sulphate by reduction to the sulphide

[14] Mond—*Berichte*—1883, p. 980.

with coal, dissolving this in water, and treating the solution with either carbon dioxide or hydrochloric acid.[15] These salts are rapidly coming into prominence as reagents for the prevention of efflorescence on brick. Efflorescence is due to the soluble salts in the clay,[16] consisting principally of the sulphates of lime, magnesia, and alkalies. These are dissolved by the water absorbed by the brick, and are finally deposited on the surface as a white scum, when the water evaporates. Of the salts commonly found in clay, only the sulphates require consideration as the cause of efflorescence on fired ware.[17] If the clay is treated with the chloride or carbonate of barium, the soluble sulphates will be converted to barium sulphate, which, on account of its extreme insolubility, cannot be brought to the surface of the brick by water. It is rather difficult to determine just how much barium should be added to a given clay, because some of it may be adsorbed by the colloidal matter. One method is to determine the amount of soluble sulphate in the clay, and add twice as much barium as is required to combine with it.[18] Or, a sample of the clay may be treated with aluminium chloride until the colloidal matter is satisfied, after which the amount of barium absorbed is taken as a direct measure of the soluble sulphates present.[19]

A method recommended for plant control requires a number of bottles of about 500 cc. capacity. In each of these is placed 100 grams of clay, either air dry or damp, and enough water added to fill the bottles about three-quarters full. They are then set in a warm place for a short time, and shaken thoroughly, until the clay has become finely divided. A one percent solution of barium chloride is then added to each bottle: one cc. in the first bottle, two cc. in the second, etc. Store in a warm place for twelve hours, with occasional shaking. Add a pinch of lime to each bottle, and, after the clay has settled, draw off 100 cc. of the supernatant liquid through a filter, and add to it a few drops of sulphuric acid. If turbidity develops, the bottle contained

[15] A. H. Fay—Barytes in Tenn.—*Eng. and Min. Jour.*, Jan., 1907, p. 137.
[16] Henrich Ries—Clay Industry of New York—*N. Y. State Museum—Bull.* 37.
[17] H. E. Ashley—Technical Control of the Colloidal Matter of Clays—*Bur. of Standards—Tech. Paper No.* 23.
[18] Seger, quoted by Kerl, Cramer and Hecht—*Handbuch der gesammte tonwaren Industrie*, 1907, p. 523.
[19] Hirsch—*Tonind. Zeit.*, Vol. 28, p. 491 (1904).

an excess of barium chloride. If, for example, the liquid from bottles 1 to 4 remains clear on the addition of sulphuric acid, while that from 5 to 10 shows turbidity, then the ratio of barium chloride to clay in bottle 5 is the proper ratio to be used in working the clay.[20] If the soluble sulphates have been extracted from the clay, their determination in the resultant dilute solution can be effected rapidly and accurately by the benzidine method, as given in detail by F. W. Buckmiller in the *Chemist Analyst,* October, 1914, p. 20.

Barium chloride is readily soluble in water; barium carbonate is not. The chloride is therefore better adapted as a reagent because a solution of it can be mixed with the clay very thoroughly and easily. On the other hand, if too much of the chloride is added, it amounts simply to the introduction of another soluble salt, and to that extent defeats its purpose. The best practice is to add nearly enough barium chloride to combine with the soluble sulphates, the rest of the barium required being added in the form of carbonate.

The values of the imports of these materials in 1913 were as follows: Natural carbonate (witherite), $13,116, duty free; manufactured carbonate, $38,949, 15 percent *ad valorem;* chloride, $37,620. duty one-quarter cent per pound.

The salts of barium have been used to some extent in a number of the ceramic industries. In the manufacture of glass they have been used to a limited extent as a substitute for lead oxide. They have the advantage over lead in that barium oxide is entirely resistant to the action of the flame gases, either oxidizing or reducing. It has a much higher fusion point than either lime or strontia, so that careful temperature regulation is not so essential. On the other hand, baryta is easily soluble in water, and glass made from it is not so resistant to the action of chemicals as lime glass. Barium is generally added to the glass in the form of carbonate, but barytes may be used if sufficient coal is added to reduce the sulphate and render it chemically active. This coal precludes the use of barytes in lead glasses, for the coal will also

[20] *Tonindustrie Kalendar,* 1908, part 2, page 99.

reduce the lead oxide, and the metallic lead formed will spot the glass.[21]

Barium has sometimes been used in the manufacture of china bodies, because of the generally accepted principle that a variety of bases tends towards a lower fusion point. Its use has little to recommend it. It seems to impart better translucency, but the bodies have only a slight range of vitrification and are apt to be weak, of poor color, shrunk, or blistered.[22]

Barium salts are also used extensively in the preparation of mat glazes.[23]

An important use of barium is in the manufacture of enamels for iron. Where tin oxide is used as an opacifier, the presence of barium is very desirable, because it tends to prevent shivering.[24] Care should be taken, however, not to heat an enamel containing any great amount of barium in direct contact with sulphurous gases. At the temperatures involved (not over 700°C.) the sulphur may combine with the barium to form soluble barium sulphide.

Barium salts when taken internally have a direct action on the muscular walls of the arteries, and will eventually cause arteriosclerosis.[25] They also act on the heart, and are apt to cause systole.[26] The chloride, sulphide, and peroxide, being soluble in water, are the most dangerous. The carbonate is soluble in the juices of the stomach, and produces the same effects. The sulphate, being quite insoluble, is practically harmless. The laborer using barium salts should be cautioned to wash his hands thoroughly before eating.

It is believed that the use of barium salts as reagents to prevent the efflorescence on brick could be extended more rapidly if the production of these salts warranted it. A study of the processes outlined above shows that it should cost but little more to manufacture barium carbonate or chloride than to refine a poor grade of barytes. In 1913, the average value of crude barytes

[21] Robert Dralle—*Die Glasfabrikation.*
[22] Herford Hope—Comparative effects of CaO, MgO, SrO, BaO, and ZnO on China Bodies.—*Trans. Amer. Cer. Soc.*, Vol. XI, 1909.
[23] Fred H. Rhead—Mat Glazes, *Trans. Amer. Cer. Soc.*, Vol. 11, 1909.
[24] R. E. Brown—Replacement of Tin Oxide in Enamels for Cast Iron, *Trans. Amer. Cer. Soc.*, Vol. XIV (1912).
[25] J. G. Adams—*Principles of Pathology*—Vol. 1, page 806.
[26] Cattell—*Lippincott's Med. Dict.*, page 969.

in the United States was $3.45 per ton; of refined barytes, $14.18. In 1912, the price paid for imported manufactured carbonate (duty included) was $21.85 per ton.[27] In November, 1914, barium chloride was quoted at from $75 to $90 a ton.[28] We have been able to discover only two plants in the United States which are equipped to manufacture the carbonate and chloride from barytes.

[27] J. M. Hill—*loc. cit.*
[28] Market report—*Jour. Ind. and Eng. Chem.*, Vol. 6, page 1051.

THE EFFECT OF SATURATED SODIUM SULPHATE SOLUTION UPON THE STRUCTURE OF CLAY BURNED TO DIFFERENT TEMPERATURES[1]

BY W. L. HOWAT, PITTSBURGH, PA.

Undoubtedly the most important quality of exposed structural stone products is their resistance to the weathering agencies, of which freezing and thawing are the most destructive. The properties which make certain materials weather-resisting, while others succumb after a shorter or longer time, are not clearly understood. It is known, of course, that a vitrified brick, showing but little absorption, endures well; but when we are dealing with porous materials, the fact stands out that the one most absorbent, showing the greatest porosity, is not always the least resistant. Thus, porous bricks made by the soft-mud process may be decidedly superior in this respect to less porous bricks made by the stiff-mud process. It is evident, that not only the volume of the pore space, but the mean diameter of the pores and their intercommunication are important factors. Bricks covered with an impervious coating like a glaze or enamel are subject to more severe stresses due to freezing and thawing, than the same grade of material not so treated.

The only means of testing structural stone products as to their resistance to atmospheric agencies has been the freezing test. It is carried out by immersing the specimens in water until saturated and then raising the water to the boiling point in order to complete the absorption. After cooling, the pieces are immersed in ice water and transferred to the refrigerator, where they are supported on gratings so that practically all faces are exposed. The specimens are then subjected to a temperature of less than 15°F. for at least five hours. They are then removed and placed in water of not less than 150°F. This operation is repeated twenty times. The absorption and loss in weight due to spalling must be determined. All visible changes are recorded,

[1] By permission of the Director, Bureau of Standards.

and on completion of this test, the samples are thoroughly dried and subjected to the transverse and compression tests. Both the appearance of the specimens as well as their physical strength, as compared with that of the samples not so treated, afford the criterion of their weather-resistance.

This test, while probably the best means of judging durability, is laborious and expensive. Other more indirect means of examination have been suggested, as for instance, the testing of specimens in the wet and dry state. Any decided lowering of the strength, due to the saturation with water, is supposed to be an index of the weather-resistance.

Accelerated tests have also been suggested as a substitute for the freezing test, by making use of the volume change due to the crystallization of salts within the pores of the material. The most important method is Brard's process[2] consisting in immersing the specimens in a boiling solution of sodium sulphate, $Na_2SO_4.10\,H_2O$, Glauber's salt, and exposing them to the air for a day in order that the salt may crystallize. This process is repeated. The solution of the decahydrate should be saturated when cold or at a temperature below 80°F. The loss in weight due to spalling may be computed. The average loss in weight by the sodium sulphate test is about six times that by the freezing test.[3] This test has also been used quite extensively by Prof. Bauschinger at the testing laboratory of the Royal Polytechnic School, Munich.

Owing to the simplicity and apparent promise of this test, it was thought desirable to apply it to burned clay, since most of the previous work was done upon stone.

For this purpose three clays were selected, "A," a calcareous buff-burning glacial surface clay, from Troy, N. Y., "B," a shale from Canton, Ohio, and "C," a No. 2 fire clay from Kittanning, Pa.

The clays were pugged thoroughly in a wet pan and run through a 3½ by 3½ inch die on a small auger machine. They were then repressed giving a finished piece approximately 4 in. by 4 in. by 2¾ in.

[2] *Ann. de Chem. et de Phys.*, Vol. 38, p. 160 (1828), later modified by d' Hericart and de Thury. *Trans. Am. Soc. C. E.*, Vol. 33, p. 246.
[3] *Trans. Am. Soc. C. E.*, Vol. 33, p. 253.

After the watersmoking and oxidation periods, the burning was carried on at the rate of 25°C. per hour, the pieces being drawn from the kiln at 50°C. intervals.

The absorptions of the pieces were next determined, after which they were dried and placed in a concentrated Na_2SO_4 solution at room temperature for 24 hours, and then in a dryer at 110°C. This treatment was repeated four times.

It was thought desirable to use the salt solution at atmospheric temperature, that is below 33°C., as above this point the solubility decreases with temperature, for it is a well-known fact that at 33°C. the decahydrate is converted into the anhydrous salt, Na_2SO_4.

Table I and Figure 1 show the results which were obtained.

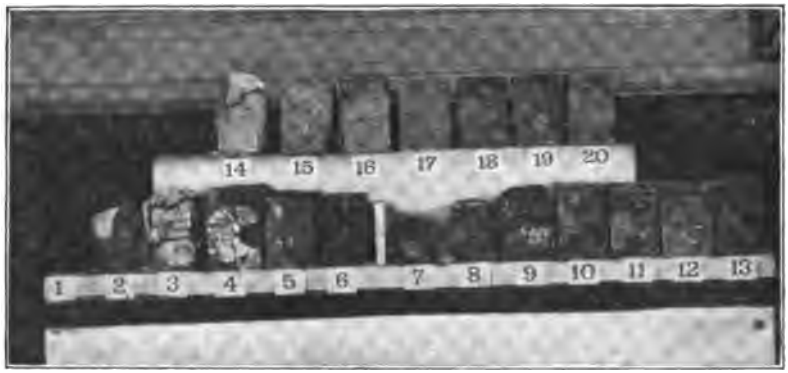


FIG. 1

In the surface clay and shale specimens, failure was preceded by the appearance of a network of cracks in the faces of the pieces, giving a sort of alligator-skin effect.

The No. 2 fire clay specimens behaved somewhat differently, in that the treatment caused the edges to crumble off—slightly at first and then to a marked degree on the following treatment. An exception can be seen in No. 17, Fig. 1, where there is a network of cracks on the face of the piece similar to those on the surface clay and shale specimens.

Thinking that too rapid cooling of the pieces when drawn from the kiln might possibly cause cracking which would affect

their ability to withstand the test, a second burn was made, in which the draw trials were quickly placed in a second kiln at dull red heat and allowed to cool down slowly. It will be noted that the absorptions of these pieces in general ran lower than those of the original pieces. This was due to the fact that the thermocouple used in this second burn was reading somewhat low, and the pieces were consequently getting more severe heat treatment. There was no noticeable difference in the effect of the Na_2SO_4 treatment on these pieces over that on the first set however, both sets having the corresponding pieces remain unaffected at the end of the fourth treatment.

A set of the pieces was also soaked in water for 24 hours and then placed outside the building to subject them to atmospheric conditions, but the freezing and thawing that they were subjected to in the course of the winter was not sufficient, owing to the moderate weather, to get any comparison between the natural and the substitute freezing tests.

It would seem from the results obtained, that in the calcareous surface clay, the temperature limit which results in material withstanding the test was not obtained accurately owing to the sudden vitrification of the material. which is typical of this type of clays. In the case of the shale, it is evident that the material becomes resistant at about 1025°C. The fire clay reaches this condition at a temperature approaching 1100°.

It has been shown that the test is sharp and decisive in breaking down the structure of clays which have not yet reached their full strength, that is. which show absorptions above about 8 percent. But while it errs on the safe side, it undoubtedly is too severe as compared with the freezing test It may, however, be possible to modify it by using a lower concentration, say a 10 percent solution of the sodium sulphate.

This work was done at the suggestion and under the direction of Mr. A. V. Bleininger.

DISCUSSION

Mr. Longenecker: These samples resemble very much some results of spalling tests. Would this test give results which would compare favorably with a spalling test?

TABLE I

NO.		TEMPERATURE CENT.	ABSORPTION	CHECK TEST ABSORPTION	REMARKS
		degrees	*percent*	*percent*	
1	Surface	900	21.7	19.4	Cracked badly on first treatment.
2		950	21.2	19.4	Failed on second treatment.
3		1000	21.2	18.0	Cracks became prominent on second treatment.
4		1050	19.1	14.8	Failed on third.
5		1100	6.3	1.3	Not affected.
6		1150	0.6	Over-burned	Not affected.
7	Shale	900	19.6	17.7	Many fine cracks after first treatment.
8		950	18.4	17.3	Failed on second treatment.
9		1000	14.2	12.0	Cracks increasing through first three treatments; failed on fourth.
10		1050	9.3	8.1	Not affected.
11		1100	2.8	3.0	Not affected.
12		1150	2.3	0.4	Not affected.
13		1200	2.7	1.3	Not affected.
14	No. 2 fire clay	900	15.8	15.3	Edges chipped after first treatment; failed on second.
15		950	15.0	15.1	Edges chipped after second treatment.
16		1000	13.5	11.6	Failed on third.
17		1050	10.5	9.6	Cracked badly on fourth treatment.
18		1100	8.2	8.3	Not affected.
19		1150	5.8	5.8	Not affected.
20		1200	3.5	3.0	Not affected.

Mr. Bleininger: I don't think so, as far as I know.

Mr. Burt: I would like to ask Mr. Bleininger if he himself has run a comparative test, freezing the samples? Did you try that?

Mr. Bleininger: Yes, sir.

Mr. Burt: How did they compare?

Mr. Bleininger: These tests are still in progress and the same samples have been left outside, all winter. They are brought in once in a while, thawed out, and exposed again.

Mr. Burt: This is going to be a more severe test?

Mr. Bleininger: It is, but some of the tests which have failed here are also failing outside, although, of course, at a much slower rate. The indications are that the test is much more severe. I certainly would not recommend it at the present time, because of its severe character.

Prof. Orton: I would like to ask Prof. Bleininger if he has correlated the sodium sulphate test with the water freezing test?

Mr. Bleininger: We had no freezing apparatus, much to our regret, and hence we were not able to carry on these tests. We hope to have one next year.

Prof. Orton: I have tried the freezing test a good many times and on a good many kinds of products. It is a very unsatisfactory method, in the fact that it requires a great number of repetitions to demonstrate whether a ware is unfit. As I understand Prof. Bleininger, this sodium sulphate test is all right for an easy case, but not for difficult cases. A water freezing test is open to the same objection. If a brick is pretty good, it may be frozen twenty-five times before any definite proof of its inability to resist is obtained. I hope this new test may prove more sharp in its action. It certainly is more convenient to ap ply, if its results are even equally as clear and decisive as the ice test, but I hope it may be more so.

Mr. Bleininger: In answer to Prof. Orton's question, our results have not been of the kind he mentioned; we obtained positive results; the only question was whether or not the test was too severe, whether or not it attacked brick which would

stand the weather all right, but would not withstand this test. Even brick that appeared quite hard were broken down by this test, bricks that appeared quite hard as far as the eye could judge, but still they were broken down by this treatment.

Prof. Orton: The principal value of this test lies in the fact that it is severe. There are few contractors that will put into a street a paving brick which they know to be of doubtful character, that is, which they know will fail from freezing, in the course of five years. These tests have shown in every case, that if the clay were carried to a sufficiently high temperature in burning, it would be resistant to this test. It seems to me, therefore, that we ought to make our test severe enough so that we will be sure that we put on the market a good product and one which cannot be questioned.

Mr. Stover: Some years ago, I tried to produce a test which could be carried out in a few days and would represent a period of several years. I adopted the boiling water test immersing for a period sufficient to get the mass thoroughly heated. I did not use a solution of ice and salt water because of the danger of absorption. I took a water pipe receptacle containing pure water, immersed within an inch or two of the top, and then did my cooling with the ice and salt, bringing it down as near as possible to the cooling test. For the twenty-five year sample, I did this for forty days and night, and the treatment was supposed to equal twenty-five years.

IMPORTANCE OF THE SAGGER-MAKING DEPARTMENT

BY GEO. SIMCOE

Too much ware is being spoiled by poor saggers, and we are breaking too many saggers. The most common causes are as follows:

1. Spalling of wash and body.
2. Spitting out of iron.
3. Bottoms warp and crack.
4. Sides warp and crack.
5. Breakage.

Why is it that all our saggers seem to go bad for a certain period and then, without any apparent cause, come good?

1. Can there be so much variation in the raw sagger clays as to cause this?

2. Do we devote too little attention to our machinery, methods of preparation, storage, unequal weathering, drying, and handling?

3 Do we have greater loss in cold weather than in hot, or greater loss in wet weather than in dry?

In order to get comparable data on this subject, I wrote to most of the potters of New Jersey and requested them to answer the list of questions as shown in Table I, which also shows the answers.

From this table, we are able to note the following:

First: Three manufacturers use 4 different clays; five manufacturers use 3 different clays; twelve manufacturers use 2 different clays and two manufacturers use one clay in their mix.

Second: Five protect their clays; 17 leave them exposed to the weather.

Third: Only one uses both ground saggers and ground pitchers for grog; the rest use ground saggers only.

Fourth: Two use $\frac{1}{8}$ inch grog, one uses $\frac{3}{8}$ inch, and the balance use $\frac{1}{4}$ inch.

Fifth: Six disintegrate their clays, the balance do not.

Seventh: Sixteen make their saggers by hand; six use hand presses, the latter being confined to the tile and electric porcelain plants.

Eighth: A body based on the averages would contain:

	percent
Tight burning plastic clay	10
Open burning plastic clay	20
Tight burning sandy clay	17
Open burning sandy clay	7
Grog	46

Ninth: The average cost of the above mix is three dollars per ton.

Tenth: The average number of fires a sagger will stand is a little better than nine.

Eleventh: Thickness of the saggers vary from ½ inch to 1⅛ inch for the sides, and ¾ inch to 1¼ inch for the bottoms.

Twelfth: The average load is from 100 to 15 pounds, neglecting superincumbent weight.

Thirteenth: The general characteristics of sagger failures seem to be cracking and breaking.

Fourteenth: The saggers are fired under different heats from cones 7 to 12.

Fifteenth: Eight manufacturers have special men in charge of their sagger department, the rest do not.

Sixteenth: Amount of breakage is 81 M. to 15 M. per year.

Seventeenth: Nine have their saggers dry before putting them in the kiln, thirteen put their saggers in wet.

Eighteenth: Eight are satisfied with their present sagger mix, the balance are not.

Nineteenth: Better sagger makers, better clays, tempering, thoroughly drying before putting in the kiln, and more attention and care in the sagger-making department are some of the needs for the production of better saggers.

Twentieth: The kilns are fired for a period of from 24 to 95 hours; they are cooled for a period of from 24 to 90 hours.

Under the heading of "Remarks," we find the following suggestions:

"Use clay as stiff as possible, and do not squeeze too quickly in the die."

"We stick many broken saggers together, and if we did not, our breakage would be greater. I do not know how this affects the actual percentage of breakage. I believe all sagger clays vary, and the variation of the clay affects the breakage. I do not know how this variation could be detected or followed up. The sizes being the same, *i. e.* length and breadth, the low sagger will break sooner than the higher one, and an oblong sagger sooner than a round one."

"The slower saggers are dried, the better."

"We consider sagger-making and the preparations of the clays are very crude. There has been no change in making, as you well know, since the first saggers were made. We should encourage the perfecting of sagger machines, and we think all clays should be pulverized and mixed with grog in that state by machinery."

"We have had saggers made of our present mix to go into and out of the kilns constantly for a year and a half, and are still in fairly good condition. There are times when we have to rush the cooling of our biscuit a little to get the ware in time for the gloss, thereby straining the saggers. However, they are quite satisfactory."

"Our experience has been, that after arriving at a satisfactory quality of clay, and using grog about ¼ inch in size, and if the saggers are made well and put on dry they will give good results, using the quality of clay at the cone we fire to. Of course, a higher temperature will result, no doubt, in a greater loss."

"We think one of the cardinal principles of improving the efficiency of saggers is the proper tempering of the mix. The present method used by the potters of tempering in the square pit does not thoroughly amalgamate the mixture, spread as it is in layers of clay, then a layer of grog, and allowed to soak for a length of time. It is then shoveled into the pug mill in very

much the same manner as it was spread into the pit, and all depends upon the closed pug for the disintegration of the material. The mix does not receive the alternate compressing and releasing action necessary to amalgamate. It is compressed and has no opportunity to expand. We have had under consideration the advisability of trying out the old brick-yard method of tempering our sagger mix in a round pit with the wheel and shaft."

From a practical money standpoint, the facts brought out in the chart show that if you break 81 M. saggers per year, you have to replace them at a cost, at a rough estimate, of 20 cents each, or 16,200 dollars.

It is interesting to note, also, that where the number of fires a sagger will stand is estimated, it is rather high as compared with actual records, which only show averages of six to seven.

When I look at my average and see that I stand up as well as the others, I am inclined to be like the eight satisfied men shown in Table I and sit back and "saw wood." However, I think with some careful and patient experimenting, we can make a great many improvements in our sagger-making department, and eventually reduce the loss.

Without attempting any further conclusions from the above analyses, let us review briefly some of the articles written on the subject:

Minton, Vol. III, *Trans. Amer. Cer. Soc.* "Refractory Materials for Glass Works," speaking of German pot clay, says it is very plastic, but has no American substitute. Its weak point is melting 7 cones lower than the other clay in the mix, yet Missouri and Pennsylvania flint clays were tested, but with poor results.

Ashley's paper on "Method of Testing Sagger Mixes," Vol. XII *Trans. Amer. Cer. Soc.*, covers very thoroughly the field of experimental sagger mixes and tests for same. He uses the quenching test on small samples to determine the value of mixes, and uses a load of 50 pounds per square inch to show their supporting value. He found that saggers made up of mixes showing high quenching test to be very satisfactory, and that sagger

mixes should contain as much coarse grog as is practical to work. A certain proportion of sandy clay with no coarser than ten mesh grains seems to add greatly to the ability to withstand sudden changes in temperature. Coarse quartz and ground ware of low absorption fail to bond properly with clays. The toughest clays available should be used for most of the mix.

Barringer found, "Strength of Sagger Bodies," Vol. XII, *Trans. Amer. Cer. Soc.*, that in testing sagger bodies, the strongest cold were the strongest hot.

Brown, Vol. XIV, *Trans. Amer. Cer. Soc.*, "Load Test on Magnesite, Chrome and Silica Brick," points out that a silica brick, with lime binder, fired on end and subjected to a load of 50 pounds per square inch stood, and was not affected at 1470°C., while one having a clay binder showed distortion at 1350°C.

Havard, Vol. XIV, *Trans. Amer. Cer. Soc.*, speaking of the recent developments in the refractory industry, mentions the use of calcined bauxite bonded with fire clay, sodium silicate, or lime. When made into brick, it has been used as lining for cement kilns and resists successfully both the heat (1600°C.) and the abrasive action.

Stout, Vol. XIV, *Trans. Amer. Cer. Soc.*, states that in no case should the plastic ingredient be such, that it will soften or vitrify near the temperature to which the ware will be subjected. It should be well above this temperature, as it fatigues quickly. Also, the amount of plastic clay should only be a thin coating, just enough to cement the grains at the points of contact and fill small voids between the flint grains. With the proper proportion of plastic clay, it will have the heat-resisting qualities of the flint. Excess of plastic clay will give the properties of plastic clay.

Parmelee, Barringer and Montgomery, Vol. XV, *Trans. Amer. Cer. Soc.*, bring out the value of talc as a refractory.

Meyer in *Metallurgical and Chemical Engineering*, Vol. XII. No. 12, published an article regarding zirconia as a new refractory. Speaking of its earlier use, he mentions that in 1880

Welsbach impregnated cotton fabric with zirconium nitrate, securing a skeleton of zirconium oxide after ignition. We are familiar with its application in gas mantles. He points out that the following formula may be used for crucibles, muffles, etc.:

75 percent 100-mesh zirconia
23 percent 10-mesh zirconia
2 percent air-slaked lime.

These are worked into a plastic mass with a three percent solution of 38° sodium silicate. The low coefficient of expansion renders zirconia ware free from danger of fracture, due to sudden changes of temperature. In this respect, it resembles fused silica ware. Owing to its high density, he recommends for lightness, that sawdust, cork dust, or certain ammonium salts be added, which will burn out and serve to lighten the product.

The cost of zirconia is considerably lower than certain artificial refractories produced in electric furnaces. In view of its remarkable properties, its cheapness should commend it strongly to the furnace man or metallurgist.

Mellor and Austin in *Clay and Pottery Industry* say that as the constituent minerals of a clay or artificial pottery body enter into combination at high temperature, new compounds are produced which will separate into a crystalline condition, when the temperature is held long enough in the zone of rapid crystallization. Fire clays also lose alkalies and alkaline earths on exposure to high temperature, so that grog after a prolonged heating is more refractory and less fusible than the original fire clay. They point out two views of the origin of brittleness in fire clay after prolonged exposure to high temperature:

1. Volatilization of alkali, whereby the clay becomes poor in fluxing or cementing agents.
2. Local contraction, with attends crystallization or devitrification.

Speaking of the Buchner ware, which is a combination of corundum and clay, they state that, after firing, the surface disintegrates though the interior remains unaffected; also, under

"fusion tests," that a manufacturer would be more simple than shrewd, if he accepted a certificate of refractoriness as a guarantee that a clay necessarily possesses all the other valuable qualities. They emphasize the fact that each clay has its own specific character and each clay accordingly must be judged by its own properties. A clay may be deficient in some qualities and possess others highly developed. A clay may be a low grade fire clay, but prove to be more satisfactory than a high grade fire clay.

Fire Clays and Fire Bricks. Many think that the higher the softening temperature of the clay, the better the quality of the fire brick. This criterion is wrong. As soon as a consumer has learned the maximum temperature likely to occur in his furnace under working conditions, then allowing something as a margin of safety, any further increase in the softening temperature of the brick frequently means that the brick will be less durable and efficient in that particular furnace. For instance, a fire brick made from too refractory a clay is more likely to have an open porous texture, which allows vapors and gases to penetrate readily into the interior. This gives rise to rapid disintegration and crumbling. An open texture brick being mechanically weak, offers also the least resistance to attack by the cutting action of flame and the slagging effects of fuel ash. Some clays vitrify at comparatively low temperatures, and yet keep their shape at comparatively high temperatures. Aluminous brick soften slowly, silicious brick rapidly.

Langenbeck, in his *Chemistry of Pottery*, has a very good article on refractory materials. He points out that potters seldom burn their saggers to a higher heat than they will meet in future use, a common practice being to burn green stock in regular ware kilns at the tops of bungs where they will usually get less heat that at any subsequent fire. His point is that if the saggers were fired to a higher heat than they would be required to stand later, better results would be obtained.

Bourry, in his *Treatise on Ceramic Industry*, under the heading "Fire Clay Goods.," p. 353, says:

"The use of silica as an opening agent modifies the chemical compositions and reduces the temperature which the material can resist. It does not allow the grains to be as coarse as is desirable, and makes the body liable to swell and even crumble in consequence of the expansion of the silica. Hence, for all best fire clay goods, only grog should be used as a non-plastic material. Fire clays which are decidedly siliceous are pure clays thinned with sand, and naturally present all the disadvantages just pointed out, and they can never be used to make fire clay goods of the highest quality. In a general way it is best to use as infusible a clay as possible, but in some cases it is advisable to use clays which, at the temperature at which they are burned, show signs of beginning to soften, as they then make the body closer and better able to resist the action of the materials with which it comes in contact in the kilns."

Havard, in *Refractories and Furnaces,* speaks of the use of coke and charcoal as a lightener for crucibles, and asbestos as having the property of holding the clay mass together, giving the following two types of such mixtures:

15 parts asbestos	3 parts fire clay
10 parts burned fire clay	2½ parts graphite
10 parts graphite	2 parts powdered asbestos
3 parts quartz	¼ parts magnesia
22 parts fire clay	½ parts quartz

Mixed with water glass and molded.

Conclusions from references:

1. Certain clays have properties other than ability to stand high temperatures that make them very valuable for saggers.
2. That silica, whether added in coarse grains as grog, or fine as sand or sandy clays is a detriment rather than a help in sagger bodies.
3. That materials other than those normally used in sagger bodies may be added with great benefit.

Based on the foregoing, I have made up the following bodies for your approval. They were all made of uniform size before firing, and were given a heat of about cone 12:

TABLE I

Mix No.	Percent by weight	Materials	Cost per ton	Cost of mix per ton
			dollars	*dollars*
1	70	Fire sand	40.00	31.00
	30	Richmond clay	10.00	
2	70	200-mesh alundum	110.00	80.00
	30	Richmond clay	10.00	
3	70	200-mesh crystolon	200.00	143.00
	30	Richmond clay	10.00	
4	70	46-mesh crystolon	200.00	143.00
	30	Richmond clay	10.00	
5	23	Short asbestos	15.00	17.66
	31	Infusorial earth	31.00	
	46	Richmond clay	10.00	
6	20	Talc	30.00	15.12
	8	Short asbestos	15.00	
	72	Edgar clay	11.00	
7	40	Zirconium oxide	111.00	51.00
	60	Edgar clay	11.00	
8	60	Calcined bauxite	40.00	28.40
	40	Edgar clay	11.00	
9	70	Calcined bauxite	40.00	31.30
	30	Edgar clay	11.00	
10	60	Fire sand	40.00	28.56
	24	Richmond clay	10.00	
	12	Short asbestos	15.00	
	4	No. 12 English ball clay	9.00	
11	56	Fire sand	40.00	24.52
	4	Short asbestos	15.00	
	8	"Dogtown Red" clay	3.00	
	32	No. 1 fire clay	4.00	
12	20	Talc	15.00	7.48
	48	Sagger grog, ¼ in	2.00	
	32	Edgar clay	11.00	

TABLE I—Continued

Mix No.	Percent by weight	Materials	Cost per ton	Cost of mix per ton
			dollars	*dollars*
13	16	Talc	15.00	
	12	Short asbestos	15.00	
	32	Fine bauxite, raw	17.00	14.44
	20	Edgar clay	11.00	
	20	V. C. 1 china clay	13.00	
14	20	Talc	15.00	
	4	Short asbestos	15.00	25.18
	48	Calcined bauxite, ⅛ in	40.00	
	28	Edgar clay	11.00	
15	15	Talc	15.00	
	8	Short asbestos	15.00	5.57
	48	Grog, 6 to 12 mesh	2.00	
	29	No. 1 fire clay	4.00	
16	60	Magnesite	50.00	
	10	Short asbestos	15.00	32.70
	30	No. 1 fire clay	4.00	
17	20	Zirconium oxide	110.00	
	10	Powdered magnesite	50.00	
	20	Powdered bauxite	40.00	
	30	8-mesh bauxite	40.00	39.23
	10	Talc	15.00	
	9	Short asbestos	15.00	
	1	40° sodium silicate	18.00	

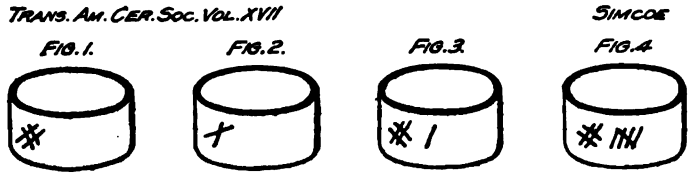
I offer these samples without comment with a hope that, in looking them over we may, by observing some characteristics that appeal to us, such as lightness, strength, texture, *et cetera,* carry home a plan of campaign that may result in better saggers for us all.

A word regarding machine-made saggers. We will hear of the many advantages of the electrically-driven press, and I can only emphasive this advantage from my own personal experience with the hand press. Between the constant cry for soft clay and laziness, it is impossible to secure the proper density. Therefore, let us see to it that our saggers are dense, if we would have them strong. We may be assured of this, if we use a power press.

It might be well to mention anothed point before closing, namely, the recent introduction of "Feurit" and "Refractorite" as a coating to be painted on the saggers, using sodium silicate as a binder. This is in line with the German process of coating vitreous ware with a refractory material, such as alumina. I tried out several saggers coated with "Feurit," but did not have encouraging results, as the coating would not keep the saggers from cracking. It may be, that if I had used a stronger and more vitreous body, my results would have been different. I hope to investigate this later.

I would like to suggest that we keep hammering at this sagger proposition until we better it. Why not make it in the order of business that we have a paper on saggers at each meeting of the Society?

Table II indicates how I keep track of the breakage in our factory. It is a monthly report of saggers broken, showing what the mix was and the characteristic sign. When saggers are made, they are marked, while green, with a nail or sharp stick as in Fig. 1. When we change the mix we change the sign as in Fig. 2.



To keep track of the number of fires the saggers stand, the kiln placers are provided with a can of Albany slip and a brush, and every time the sagger goes in the kiln they make marks as in Figs. 3 and 4. If the drawers break a sagger beyond repair, then by counting the number of Albany slip marks, they can tell the number of times it has been fired and by the scratched in sign what mix it was, thus the sagger in Fig. 4 has been fired five times. The drawers and placers have pads marked so they can keep track of breakage according to above, and turn the same in to the foreman each week. From this weekly report he compiles the monthly sheets. From this you will see that we not only get

TABLE I

	QUESTIONS	ELECTRIC PORCELAIN			TILE					GENERAL WARE		
		No. 1	No. 2	No. 3	No. 1	No. 2	No. 3	No. 4	No. 5	No. 1	No. 2	No. 3
1	How many different clays do you use in your sagger mix?.....	2	2	2	3	2	1	2	2	2	2	1
2	Do you store said clays in bins exposed to, or protected from the weather?	Exp.	Exp.	Exp.	Exp.	Exp.	Exp.	Pro.	Exp.	Exp.	Exp.	Exp.
3	Do you use ground saggers or ground pitchers for grog?.....	Sag.	Sag.	Both	Sag.	Sag.	Sag.	Sag.	Sag.	Sag.	Sag.	Sag.
4	What is the average size of grog used?	3/16 in.	1/4 in.	....	3/16 in.	1/4 in.	1/4 in.	1/4 in.	3/16 in.	1/8 in.	3/16 in.	1/4 in.
5	Do you disintegrate your raw sagger clays before putting them in the soaking pit?.....	No	No	No	No	No	No	Yes	No	Yes	No	No
6	Do you pug twice?.....	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	3
7	Are your saggers made by hand or machine? If machine, please describe	Hand	Press	Press	Press	Press	Hand	Press	Press	Hand	Hand	Hand

TABLE I—Continued

	QUESTIONS	ELECTRIC PORCELAIN			TILE					GENERAL WARE		
		No. 1	No. 2	No. 3	No. 1	No. 2	No. 3	No. 4	No. 5	No. 1	No. 2	No. 3
8	Please give percentage by volume of materials in your sagger mix, according to the following (at cone 12):	percent	percent	percent		percent	percent	percent	percent	percent	percent	percent
	Tight burning plastic clay.....	5	..	33	..	38	..	..	..	..	..	..
	Open burning plastic clay.....	15	30	..	..	..	50	25	35	40	25	..
	Tight burning sandy clay.....	15	..	33	..	26	..	25	15	10	..	50
	Open burning sandy clay.....	15	30	..	..	..	..	..	..	..	19	..
	Grog	50	40	34	..	36	50	50	50	50	56	50
9	How much does the above mix cost per ton, not counting labor?	2.72	3.00	3.00	3.25	3.25	4.00	....	4.00	3.25	1.47	4.50
10	How many fires will saggers made from the above mix stand?	....	7	12	5	19	15	16	....	....	14	8
	How did you obtain these figures?	....	Rec.	Est.	Est.	Est.	Est.	Est.			Est.	Est.
11	What are the dimensions of your average sagger in cu. in., and thickness of sides and bottom?	810 ⅞S 1¼B	750 1 in. 1 in.	.... 1 in. 1 in.	1064 1 in. 1 in.	560 ⅞ in. ⅞ in.	 1 in. 1 in.	630 1 in. 1 in.	504 1 in. 1 in.	3344 1 in. ¾ in.	6384 ½ in. ¾ in.	5984 ....

12	What is the average load these saggers have to bear?.....	25	25	15	24	....	40	60	....	....	....	15
13	What are the general characteristics of sagger failures?.....	Crack	Crack	Crack	....	Crack	Crack	Break	Break	....	Break	....
14	What heat do your saggers get, in terms of cones?	12	12	10	10	10	8	12	12	9	9	7
15	Do you have a special man in charge of your sagger department?	No	No	Yes	Yes	Yes	No	Yes	No	No	No	No
16	How many saggers do you break per year?	....	28M.	50M.	15M.	....	....	....	....	50M.	....	....
17	Are your saggers thoroughly dry when they go in the kiln? How do you know?.....	No	No	No	Yes	No	Yes	No	No	No	Yes	No
18	Are you satisfied that the saggers you are using are as good as can be produced to meet your special conditions?	....	No	No	Yes	No	Yes	Yes	No	No	No	Yes
19	What, in your judgment, is needed for the production of better saggers?	....	More attention	....	....	Better men	....	....	....	Men	Method	Drying
20	How long do you fire your kilns?	75hrs.	24hrs.	36hrs.	....	80hrs.	72hrs.	50hrs.	95hrs.	48hrs.	60hrs.	....
	How long do you cool your kilns?	48hrs.	24hrs.	24hrs.	....	60hrs.	90hrs.	....	72hrs.	....	48hrs.	....

TABLE I—Continued

	QUESTIONS	SANITARY										
		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10	No. 11
1	How many different clays do you use in your sagger mix?.....	2	3	2	4	3	3	4	2	3	2	4
2	Do you store said clays in bins exposed to, or protected from the weather?	Pro.	Pro.	Pro.	Exp.	Exp.	Pro.	Exp.	Exp.	Exp.	Exp.	Exp.
3	Do you use ground saggers or ground pitchers for grog?.....	Sag.	Sag.	Sag.	Sag.	Sag.	Sag.	Sag.	Sag.	Sag.	Sag.	Sag.
4	What is the average size of grog used?	—	¼ in.	¼ in.	¼ in.	¼ in.	¼ in.	¼ in.	⅛ in.	¼ in.	⅜ in.	¼ in.
5	Do you disintegrate your raw sagger clays before putting them in the soaking pit?.....	No	No	Yes	No	Yes	No	No	Yes	No	Yes	No
6	Do you pug twice?.....	Yes	1	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
7	Are your saggers made by hand or machine? If machine, please describe	Hand	Hand	Hand	Hand	Hand	Hand	Hand	Hand	Hand	Hand	Hand

8	Please give percentage by volume of materials in your sagger mix, according to the following (at cone 12):	*percent*	*percent*		*percent*	*percent*	*percent*	*percent*		*percent*		*percent*
	Tight burning plastic clay.....	..	..	..	40	28	20	..	..	28	..	24
	Open burning plastic clay.....	20	33	..	30	..	10	37	..	..	20	29
	Tight burning sandy clay.....	30	33	..	15	22	..	13	..	..	33	..
	Open burning sandy clay.....	..	..	..	15	..	30	..	..	22	..	..
	Grog	50	34	..	40	50	40	50	..	50	47	47
9	How much does the above mix cost per ton, not counting labor?	3.50	2.84	8.00	3.00	3.00	2.00	2.75	3.25	....	....	3.00
10	How many fires will saggers made from the above mix stand?	8	6	....	6	....	7	13	....	5	7	5
	How did you obtain these figures?	Est.	Rec.		Rec.		Rec.	Est.		Est.	Est.	Est.
11	What are the dimensions of your average sagger in cu. in., and	4256	4091	4320	....	5434	....	3696	3780	5513	....	5280
	thickness of sides and bottom?	....	⅞ in.	....	....	¾ in.	¾ in.	1⅛ in.	1 in.	....	1 in.	1 in.
		....	⅞ in.	....	....	¾ in.	1 in.	1⅛ in.	1 in.	....	1 in.	1 in.
12	What is the average load these saggers have to bear?.....	86	40	75	150	500	60	....	45	100	100	60
13	What are the general characteristics of sagger failures?.....	Crack	Crack	....	....	Crack	....	....	Crack	Crack	Crack	Crack

TABLE I—Continued

	QUESTIONS	SANITARY										
		No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10	No. 11
14	What heat do your saggers get, in terms of cones?	10	9	8	9	9	9	7	9	11	9	10
15	Do you have a special man in charge of your sagger department?	Yes	Yes	No	Yes	No	Yes	No	No	No	No	No
16	How many saggers do you break per year?	....	81M.	....	....	....	....	15M.	....	....	....	....
17	Are your saggers thoroughly dry when they go in the kiln? How do you know?.....	Yes	No	No	Yes	No	Yes	No.	Yes	Yes	No	Yes
18	Are you satisfied that the saggers you are using are as good as can be produced to meet your special conditions?	Yes	No	No	No	No	Yes	Yes	Yes	No	No	No
19	What, in your judgment, is needed for the production of better saggers?	Clay	Clay	....	....	Care	Men	....	Clay	Men	Temper	Men
20	How long do you fire your kilns?	60hrs.	42hrs.	....	62hrs.	48hrs.	....	40hrs.	....	53hrs.	55hrs.	52hrs.
	How long do you cool your kilns?	60hrs.	48hrs.	....	66hrs.	60hrs.	....	48hrs.	....	....	60hrs.	70hrs.

a fairly accurate report of our yearly breakage, but also are able to see which will stand up the best.

In conclusion, I wish to thank the gentlemen who so kindly answered the list of questions and helped to make this paper possible.

TABLE II—KILN REPORT SAGGER BREAKAGE

5 WHEELBARROWS SANDY RED CLAY
5 WHEELBARROWS FIRE CLAY
150 SHOVELS GROG

NEW DIE—MACHINE REPAIRED DECEMBER 31, 1912.

DEC.	NUMBER OF FIRINGS																
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
1	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
2	...	...	...	...	...	...	2	3	...	1	...	...	...	...	...	...	...
3	...	...	...	...	...	6	5	3	4	3	3	5	3	2	3	...	...
4	...	...	2	4	...	1	4	4	...	1	4	...	3	...	3	...	3
5	1	.5	2	4	4	6	4	4	4	4	3	3	4	...	...	...	...
6	...	...	...	...	...	...	6	...	5	9	...	6	4	3	2	...	...
7	...	...	...	...	2	4	2	3	5	4	4	2	3	2	...	...	...
8	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
9	...	...	2	...	1	1	...	4	2	4	...	3	4	2	2	...	...
10	...	3	...	...	2	...	2	5	4	4	3	4	4	3	...	...	...
11	5	2	1	6	5	5	3	6	10	6	4	6	5	6	4	...	...
12	6	3	1	4	6	9	6	6	2	4	4	4	4	3	3	...	...
13	5	1	4	5	7	6	4	6	5	3	3	3	3	3	2	...	...
14	6	2	6	3	6	10	16	10	12	7	3	4	3	1	...	...	...
15	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
16	...	...	...	...	...	...	7	6	9	6	7	7	13	6	...	...	...
17	5	3	2	3	6	...	4	10	10	10	8	8	8	3	...	...	...
18	2	...	...	1	7	10	7	10	8	10	8	10	15	8	6	...	...
19	4	...	2	4	7	4	9	6	7	8	12	11	6	3	...	...	...
20	...	...	...	...	1	2	6	6	10	6	3	7	5	4	1	...	...
21	...	...	...	...	2	...	9	7	7	5	8	9	8	4	2	...	...
22	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
23	...	...	...	...	...	2	6	5	10	9	6	7	6	2	...	...	...
24	4	1	...	4	10	6	8	8	8	7	5	11	12	11	8	...	...
25	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
26	4	...	...	5	2	2	8	5	5	7	6	11	9	7	3	...	...
27	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
28	...	...	...	4	5	1	4	7	5	6	6	6	9	2	1	...	...
29	...	...	...	2	4	4	6	7	8	6	6	7	9	8	3	...	...
30	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
31	...	...	...	...	...	...	8	8	2	9	5	6	6	5	...	...	...
Total	42	20	22	49	78	79	136	140	138	139	110	140	146	88	43	...	3

THE PRESENT STATUS OF THE PRODUCER GAS FIRED CONTINUOUS KILN IN AMERICA[1]

DISCUSSION CONTRIBUTED AFTER PUBLICATION OF VOLUME XVI

Mr. McElroy: I will take up Mr. Richardson's discussion, point by point, as he made it. In his first paragraph he is particular to point out that the gas producer, which we mentioned in our paper, is not the only gas producer of that type in the United States, which is perfectly true. It was not the intention of the authors, in any sense of the word, to say that they were connected with the only pressure producer that would work. As a matter of fact, the reason we brought this up in our former paper, was to show how the troubles Mr. Richardson had were overcome in a great measure by means of the new pressure producer; and, as we were closely associated with the firm which first tried the pressure producer in connection with the gas fired kiln, we wanted to give the Society the benefit of our experience in that line.

We note that Mr. Richardson thinks that the pulling of the combustion gases, three, five and six chambers ahead of the fire is not the best practice. Possibly he has found in his experience that it is not. Our experience has been, that the greater the number of chambers that we can pull the product of combustion through, ahead of the fire, the more gradual will each chamber heat up, and therefore the greater the benefit to tender clays. We had one instance not long ago in Toronto, where we had all kinds of checking in the use of a calcareous surface clay, and by pulling the products of combustion through one more chamber, the trouble was entirely eliminated. He thinks possibly it might scum the ware with such practice. I have never seen it do it, owing to the fact that the chambers just mudded up are preheated by pure hot air instead of combustion gases.

[1] See *Trans. Amer. Cer. Soc.*, Vol. XVI, page 585. Mr. McElroy's illness at the time of the publication of Vol. XVI prevented further discussion of this paper.

He notes as remarkable, our statement that there is one 15 chamber kiln in the United States which is not using fires at the end where the return is made; I mean by this a single battery type of kiln. It is indeed remarkable; there is no question about it. but it is being done, and done in Tennessee. I am not at liberty to publicly announce the firm's name that is doing it, yet I will be glad to do so in private, if anyone cares to know.

Mr. Richardson states they, referring to the authors, "may modify to some small degree the design of the kiln for special conditions, but it is well known that patent kiln promoters sell their particular type of kiln to every one that they can persuade to adopt it and who are able to pay their charges." Now this is a matter that I must refute. There is no question that in past times, 10, 15, 20 years ago, this was the common method of doing business in all lines of business, but at present, the firms that start out to do business in this particular way will soon go to the wall. The only way, business can be done now, is in an honest way, and the firm that does not have as its motto, "Business is Service." is bound to go to the wall soon. As a matter of fact, you take a compartment continuous kiln, there are certain kinds of chambers, certain operations in the kiln which must be used upon every yard. The clay itself determines what the size of this chamber shall be, how the gas ports shall be placed, what the number of chambers shall be and all that. At present, so far as I know, in the designing of all continuous kilns, this is being particularly investigated, and a kiln is placed on a yard to meet the particular conditions on that yard.

Mr. Richardson further states: "Their business is not in designing or recommending, as engineers would do, a kiln to meet the local conditions in any special case, but their efforts are all directed to the single type of kiln, the producer gas fired kiln." Now, as a matter of fact, we are sure that Mr. Richardson did not mean this as you would read it, for the reason that Mr. Richardson is at present endeavoring to place a patent gas fired kiln on the market, and this would necessarily place him in the same category as he would place us, which I do not believe he means to do. He further states that they, re-

ferring to us, the authors of the paper: "are hired for this, and their employer rates them by their ability to do this." We must emphatically refute this. As we said before in the other remarks, we do not believe that the gentleman really meant what that conveys. You go through the records of the Society in past years, and you will find very few articles brought out by the large equipment firms in the country. Why? For the simple reason that the equipment firms were afraid that their motives in bringing these articles before the Society would be questioned. They were afraid that the Society would stamp them as advertising their articles. As a matter of fact, in this particular case, the authors were several months, in fact several years, in getting our associates to allow us to present this paper before the Society, and we are very sorry indeed that our motives have been questioned in this regard. The continuous kiln business at the present time in the country is a large one. The gas fired kiln business alone represents an investment in 45 kilns of 1,000,000 to 2,000 000 dollars, and that means something. It means that it is an established proposition and therefore must be taken up and met by the Society, and that is what we try to convey in our paper, and I am very sorry indeed that our motives were questioned in this regard.

Mr. Richardson further states: "As to the advantages of the producer gas fired kiln, most of them are applicable to any good continuous kiln, for low priced products to a greater degree with the coal fired than with the producer gas fired kiln." It is an established fact, in which Mr. Richardson agrees with us, that for very good products, higher class products, the gas-fired kiln is better than the coal-fired, continuous kiln; but we must disagree with him on the low product proposition, because for low priced products, the gas fired kiln used at present is of the tunnel variety, a kiln practically similar to all continuous coal-fired kilns in construction, with the exception that it is gas-fired by means of producers. Approximately 1,500 dollars extra expense will put a gas-fired kiln on the same yard, that a coal-fired kiln could be put on for the burning of low grade products, and this would be a good investment because of the fact that in a gas fired

kiln, the product is freer from discoloration than in kilns which are coal fired. The producer gas proposition is one that is coming to the front rapidly. Experiments are now being carried on, which look very much as if, in the near future, an entire plant will be fired by producer gas starting from the boilers, through the dryers to the kiln.

CHROME-TIN RED GLAZES BETWEEN CONES 2 AND 8

BY B. S. RADCLIFFE AND C. L. WALDUCK

The production of chrome-tin reds has been confined in most instances to temperatures between Seger cones 04 and 2. The stoneware manufacturers, although desirous of producing reds at their temperatures, have failed in practically every instance to produce a deep uniform red. It was, therefore, decided to investigate the most promising portion of the glaze field within temperature ranges of cones 6 to 8 which is the heat range generally used for maturing stoneware, and develop; if possible, a good commercial color. Owing to some interesting developments, it was later decided to include glazes maturing at lower temperatures. The results obtained were very gratifying, but the writers realize that they have only made a start in the investigation, and that further work along similar lines would in all probability bring out many interesting and valuable facts.

A brief review of the published articles on chrome-tin colors revealed the following points:

1. Source of chromium best suited for the production of the chrome-tin color: Seger[1] and Carter[2] used potassium dichromate ($K_2Cr_2O_7$) and Hull[3] used chromic acid (CrO_3). Purdy[4] (from whose work the stain composition used in the following work was selected) used various compounds of chromium and stated that different results are obtained with different chromium compounds.

2. Influence of calcium on the chrome-tin color: Seger[1] found that if the lime is decreased, the color tends toward lilac and if excluded toward pink. Hensel[5] found that a reduction of lime weakened the color.

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[1] *Trans. Amer. Cer. Soc.*, Vol. IV, p. 231.
[2] *Ibid*, Vol. V, p. 242.
[3] *Trans. Amer. Cer. Soc.*, Vol. IV, p. 233.
[4] *Ibid*, Vol. XI, p. 228.
[5] *Trans. Amer. Cer. Soc.*, Vol. V, p. 245.

Outline of Work. Thorough investigations were made by Purdy[6] on chrome-tin stains, and he reported very good reds with composition—1 SnO_2, 1 SiO_2, .075 $PbCrO_4$ and 2 to 2.5 CaO. Therefore, it was decided to use 2.25 CaO, keeping the other constituents of the stain as above. This stain was used throughout the investigations, an amount of the stain sufficient to introduce .118 equivalents of SnO_2 being added to all glazes. All glazes, therefore, contained the same molecular quantities of the components of the stain which is shown by the formula:

$$\left.\begin{matrix} .2660\ CaO \\ .0088\ PbO \end{matrix}\right\} .0088\ Cr_2O_3 \left\{\begin{matrix} .118\ SiO_2 \\ .118\ SnO_2 \end{matrix}\right.$$

The work was designed to determine:

First, the alumina-silica ratio best suited for glazes at stoneware heats (cone 6 to 8).

Second, the effect of different glaze composition on the stain at temperatures corresponding to cones 2, 4 and 8, keeping the alumina and silica constant and varying the boracic acid, and the lead oxide, calcium carbonate and barium carbonate in the R O.

The limits used by Purdy[7] to produce a red from cone 01 to 3 are:

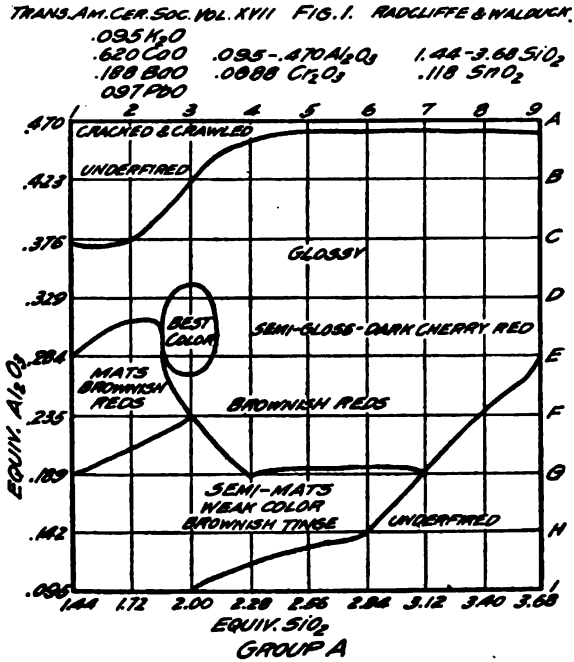
First, the stain shall contain 1 equivalent each of tin oxide (SnO_2) and silica (SnO_2)—2.25 equivalents of calcium oxide and .075 equivalents of chromium oxide; second, the chromium shall be derived from lead chromate ($PbCrO_4$); third, the stain shall be calcined to cone 8 and then washed; and fourth, each glaze shall contain .1 equivalent of stain thus introducing .1 equivalent of tin oxide (SnO_2).

Since the volatility of Cr_2O_3 increases with increase in temperature, the molecular equivalent of the stain was increased to .118 to suit the higher temperatures employed in this work.

The Stain. The materials used in the stain were weighed according to the following batch weights:

[6] *Ibid*, Vol. XI, p. 282.
[7] *Trans. Amer. Cer. Soc.*, Vol. XI, p. 281.

	grams
Tin oxide	622.4
Flint	247.6
Whiting	930.0
Lead chromate	200.0
	2000.0



The batch was screened dry, through a 60 mesh sieve several times and well mixed. The mixture was placed in a fire clay sagger and calcined to cone 8 in 20 hours. A fairly uniform distribution was secured by this heat treatment, and factory conditions closely approximated. The stain was then washed, decanted twice and dried. The dry stain is brownish red in color.

THE GLAZES

Group A. The first group of glazes was made to obtain a glaze which had the most suitable Al_2O_3:SiO_2 ratio for cones 6

to 8 heats. The RO constituents and the stain were kept constant, and the Al_2O_3 and SiO_2 were varied as shown in Fig. 1. The molecular formulae of the four corner glazes are:

$$A_1 \quad \left.\begin{matrix}.095\ K_2O \\ .620\ CaO \\ .188\ BaO \\ .097\ PbO\end{matrix}\right\} \left.\begin{matrix}.4700\ Al_2O_3 \\ .0088\ Cr_2O_3\end{matrix}\right\} \left.\begin{matrix}1.440\ SiO_2 \\ 0.118\ SnO_2\end{matrix}\right.$$

$$A_9 \quad \left.\begin{matrix}.095\ K_2O \\ .620\ CaO \\ .188\ BaO \\ .097\ PbO\end{matrix}\right\} \left.\begin{matrix}.4700\ Al_2O_3 \\ .0088\ Cr_2O_3\end{matrix}\right\} \left.\begin{matrix}3.680\ SiO_2 \\ 0.118\ SnO_2\end{matrix}\right.$$

$$I_1 \quad \left.\begin{matrix}.095\ K_2O \\ .620\ CaO \\ .188\ BaO \\ .097\ PbO\end{matrix}\right\} \left.\begin{matrix}.0950\ Al_2O_3 \\ .0088\ Cr_2O_3\end{matrix}\right\} \left.\begin{matrix}1.440\ SiO_2 \\ 0.118\ SnO_2\end{matrix}\right.$$

$$I_9 \quad \left.\begin{matrix}.095\ K_2O \\ .620\ CaO \\ .188\ BaO \\ .097\ PbO\end{matrix}\right\} \left.\begin{matrix}.0950\ Al_2O_3 \\ .0088\ Cr_2O_3\end{matrix}\right\} \left.\begin{matrix}3.680\ SiO_2 \\ 0.118\ SnO_2\end{matrix}\right.$$

The batch weights of the above are:

	A_1	A_9	I_1	I_9
	grams	*grams*	*grams*	*grams*
Feldspar	389.9	334.2	445.6	334.2
Whiting	262.5	225.0	300.0	225.0
Barium carbonate ..	276.5	237.0	316.0	237.0
White lead	180.6	154.8	206.4	154.8
Raw clay,				
Tenn. No. 7.....	225.75	193.5	.....	.....
N. C. kaolin	135.45	151.1	.....	.....
Calcined N. C. kaolin	361.20	309.6	.....	.....
Flint	.....	864.0	384.0	1152.0
Stain	339.08	290.64	387.52	290.64
	2170.98	2724.84	2039.52	2393.64

The glazes were blended so that there were 100 grams of material in each.

The batch weights calculated directly from the molecular formulas of the glazes are:

	A_1	A_3	I_1	I_3
Feldspar	53	53	53	53
Whiting	62	62	62	62
Barium carbonate	37	37	37	37
White lead	25	25	25	25
Clay	97	97	..	..
Flint	7.2	142	52	187
Tin oxide	17.8	17.8	17.8	17.8
Chromium oxide	5.7	5.7	5.7	5.7
	304.7	439.5	252.5	387.5

The four corner glazes were made up and ground in ball mills for two hours, removed, screened, the water factor determined and the blending weights calculated. Two trials of each glaze were made, and applied to U. S. Encaustic tile. The trials were burned to cone 7 in an oil-fired, down-draft test kiln, the period of the burn being 12 hours. Oxidizing conditions were maintained throughout the burn.

The results obtained in this group and shown in Fig. 1 were quite encouraging. All are red but have a brownish tinge, with the exception of E_3 which is a dark cherry-red. It is a semi-glossy glaze, but when applied to a stoneware body and burned to cone 8, it produces a bright glossy glaze that fits well. The glazes containing high clay cracked during drying. The good mats and glossy glazes showed no signs of cracking after dipping, no crazing, crawling or shivering after burning. They fit very well. The best glaze is E_3.

In chrome-tin red glazes the Al_2O_3-SiO_2 ratio has a decided effect upon the color as is shown in Fig. 1 In this work the best red was obtained with an Al_2O_3-SiO_2 ratio of 1:7.

Group B. The Al_2O_3-SiO_2 ratio of E_3 was taken as the most suitable to use for further investigation, and a second group B consisting of 15 glazes was made having this ratio constant and a variable R O and a varied boracic acid content. Group B is

a triaxial in form having for its corners the three following glazes as shown by their molecular formulas:

A_1

$$\left.\begin{matrix}.189\ K_2O \\ .716\ CaO \\ .095\ BaO\end{matrix}\right\} \left.\begin{matrix}.2840\ Al_2O_3 \\ .4730\ B_2O_3 \\ .0088\ Cr_2O_3\end{matrix}\right\} \left.\begin{matrix}2.000\ SiO_2 \\ 0.118\ SnO_2\end{matrix}\right.$$

E

$$\left.\begin{matrix}.189\ K_2O \\ .473\ PbO \\ .338\ CaO\end{matrix}\right\} \left.\begin{matrix}.2840\ Al_2O_3 \\ .0088\ Cr_2O_3\end{matrix}\right\} \left.\begin{matrix}2.000\ SiO_2 \\ 0.118\ SnO_2\end{matrix}\right.$$

E_5

$$\left.\begin{matrix}.189\ K_2O \\ .716\ CaO \\ .095\ PbO\end{matrix}\right\} \left.\begin{matrix}.2840\ Al_2O_3 \\ .0088\ Cr_2O_3\end{matrix}\right\} \left.\begin{matrix}2.000\ SiO_2 \\ 0.118\ SnO_2\end{matrix}\right.$$

One-half of glaze A containing all of the boracic acid was fritted. The molecular formula of the frit is as follows:

$$\left.\begin{matrix}.3\ K_2O \\ .2\ BaO \\ .5\ CaO\end{matrix}\right\} \left.\begin{matrix}0.30\ Al_2O_3 \\ 1.00\ B_2O_3\end{matrix}\right\} \left.\begin{matrix}2.10\ SiO_2\end{matrix}\right.$$

Combining weight 314.1.

Batch Weight

Potash feldspar	157.5
Barium carbonate	39.4
Calcium carbonate	50.0
Flint	18.0
Boracic acid	124.0
	398.9

The frit was mixed dry by screening several times through a 60 mesh screen, melted in a down-draft frit furnace and quenched in cold water as it ran out of the bottom of the crucible. It was then ground wet in a ball mill to pass a 100 mesh screen.

The batch weights of group B.

	A	E	E_5
White lead	.....	128.8	25.8
Frit	157.05	.....	.....
Feldspar	29.9	111.6	111.6
Clay—Tenn. ball clay No. 7	25.8	25.8	25.8
Flint	27.0	36.0	36.0
Whiting	22.5	7.5	47.5
Stain	48.4	48.4	48.4
	308.69	358.14	295.14

The batches were weighed and ground in ball mills for two hours. The water factor was determined, and the glazes blended according to Fig. 2. Three sets of these glazes were dipped on U. S. Encaustic tile and burned in 12 hours to cones 8, 4 and 2.

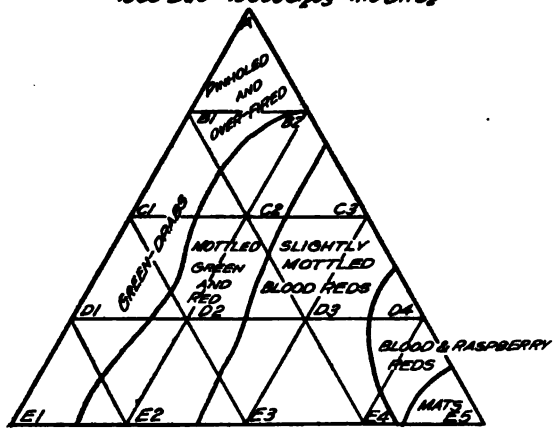
Cone 8 Burn. The results are shown in Fig. 2. This burn produced some good colors. As the B_2O_3 and Pb_3O_4 increase, the red changes to a sea-gull green drab. These greens showed small pinholes due to the formation of gas and probably a second boiling due to overfiring. D_4 is the best glossy glaze. It has a dark raspberry red color. The glaze is opaque and does not craze or crawl.

Cone 4 Burn. This burn, as is shown in Fig. 3, produced a wider field of red colors. The lower heat did not dissociate the chrome-tin compound, producing greens as much as it did in the cone 8 burn. Nevertheless there was some green present, as in glaze A, where the red color was mottled with green. D_3 is the best glaze with a color between a raspberry red and cherry red, but D_2 has the best color—blood red.

Cone 2 Burn. Results are shown in Fig. 4. All of the glazes burned at this temperature are free from green color; those high in boracic acid and lead are slightly over-fired, and with the exception of E, show a mottled effect due to a partial second boiling of the glaze. They probably mature at cone 01 to 1. The mottled effect decreases from A to E, which shows that the boracic acid glaze is more susceptible to a second boiling

TRANS. AM. CER. SOC. VOL. XVII FIG. 2. RADCLIFFE & WALDUCK

$.189\,K_2O$ $.284\,Al_2O_3$
$.716\,CaO$ $.473\,B_2O_3$ $2.00\,SiO_2$
$.095\,BaO$ $.0088\,Cr_2O_3$ $.118\,SnO_2$

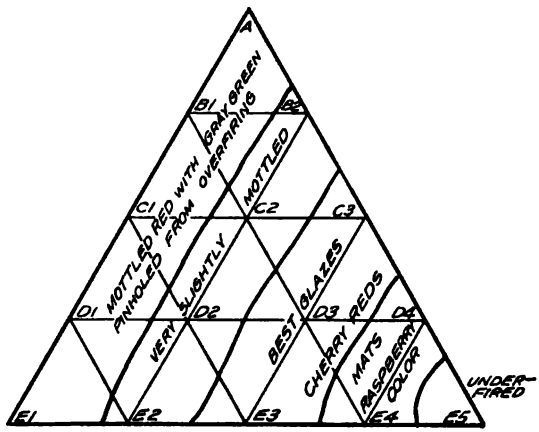


$.189\,K_2O$
$.338\,CaO$ $.284\,Al_2O_3$ $2.00\,SiO_2$
$.473\,PbO$ $.0088\,Cr_2O_3$ $.118\,SnO_2$

$1.89\,K_2O$
$.716\,CaO$ $.284\,Al_2O_3$ $2.00\,SiO_2$
$.095\,PbO$ $.0088\,Cr_2O_3$ $.118\,SnO_2$

GROUP B
CONE 8 BURN

TRANS. AM. CER. SOC. VOL. XVII FIG. 3. RADCLIFFE & WALDUCK



GROUP B
CONE 4 BURN

than the lead glaze. C_2 is the best glaze. It is opaque and shows no defects.

Glaze E_5 was applied to a piece of biscuit stoneware and burned to cone 8. It retained a good red color, had a good gloss and fitted very well.

Best Glazes and Molecular Formulas

Group B

Cone 8 Burn.

D_4

$$\left.\begin{matrix}.1890\ K_2O \\ .7160\ CaO \\ .0713\ PbO \\ .0238\ BaO\end{matrix}\right\} \left.\begin{matrix}.2840\ Al_2O_3 \\ .1183\ B_2O_3 \\ .0088\ Cr_2O_3\end{matrix}\right\} \left.\begin{matrix}2.000\ SiO_2 \\ 0.118\ SnO_2\end{matrix}\right.$$

Cone 4 Burn.

D_3

$$\left.\begin{matrix}.1890\ K_2O \\ .6215\ CaO \\ .1656\ PbO \\ .0238\ BaO\end{matrix}\right\} \left.\begin{matrix}.2840\ Al_2O_3 \\ .1183\ B_2O_3 \\ .0088\ Cr_2O_3\end{matrix}\right\} \left.\begin{matrix}2.000\ SiO_2 \\ 0.118\ SnO_2\end{matrix}\right.$$

Cone 2 Burn.

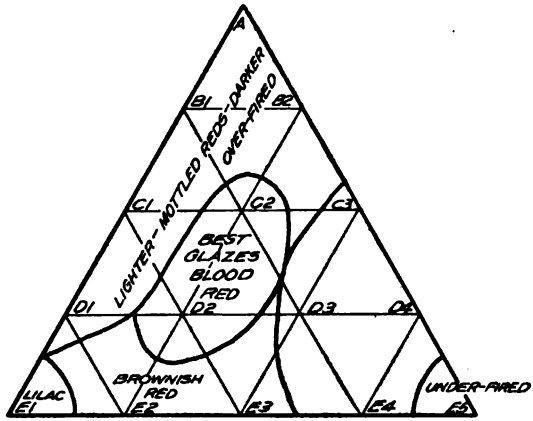
C_2

$$\left.\begin{matrix}.1890\ K_2O \\ .6215\ CaO \\ .1419\ PbO \\ .0476\ BaO\end{matrix}\right\} \left.\begin{matrix}.2840\ Al_2O_3 \\ .2366\ B_2O_3 \\ .0088\ Cr_2O_3\end{matrix}\right\} \left.\begin{matrix}2.000\ SiO_2 \\ 0.118\ SnO_2\end{matrix}\right.$$

(1.) In Group B, good red colors can be made, using chrome-tin stain as a coloring agent, between cones 2 and 8, provided the proper maturing glaze for that temperature is used.

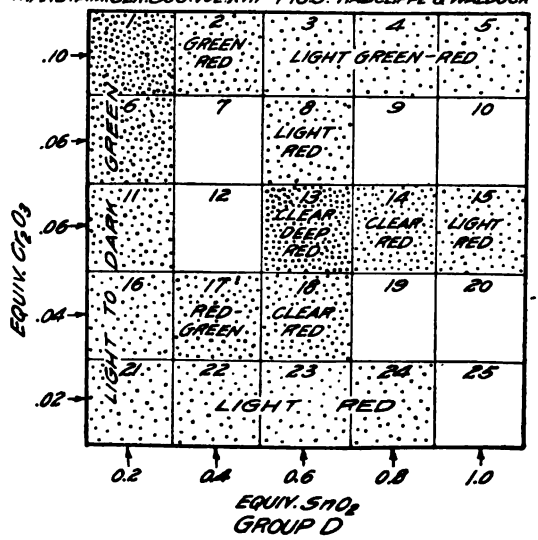
(2.) With Al_2O_3 and SiO_2 constant, an increase of B_2O_3 changes the color from a raspberry red to a cherry red. In the over-burned glazes containing boracic acid, a second boiling or evolution of gas takes place, and at this time dissociation of the chrome-tin stain occurs, with a result that a light green or mottled green mixed with red is developed, depending on the extent of the over-firing and consequent dissociation.

TRANS. AM. CER. SOC. VOL. XVII FIG. 4. RADCLIFFE & WALDUCK



GROUP B
CONE 2 BURN

TRANS. AM. CER. SOC. VOL. XVII FIG. 5. RADCLIFFE & WALDUCK



GROUP D

(3.) Glazes in which lead replaces calcium, show color changes from a raspberry red to a lilac when properly matured. In over-fired glazes, lead has practically the same effect as boracic acid, namely, the production of green or mottled green and red colors.

Group C. Five glazes were made in which .2 CaF_2, .2 MgO, .2 BaO and .2 Bi_2O_3 were substituted for CaO in the glaze:

$$\left.\begin{matrix} .189\ K_2O \\ .716\ CaO \\ .071\ PbO \\ .024\ BaO \end{matrix}\right\} \left.\begin{matrix} .2840\ Al_2O_3 \\ .1180\ B_2O_3 \\ .0088\ Cr_2O_3 \end{matrix}\right\} \left.\begin{matrix} 2.000\ SiO_2 \\ 0.118\ SnO_2 \end{matrix}\right\}$$

The introduction of CaF_2 had no perceptible effect on the color, a duller and seemingly more refractory glaze was produced, however. The glaze containing .2 MgO is mottled white and red. The addition of BaO changes the color from the deep cherry red to a brownish red. Bi_2O_3 made a more easily fusible glaze of a mottled green and red color.

It follows, therefore, that the R O of a glaze has a very decided effect upon the color of chrome-tin glazes.

Group D. A series of 25 stains were made having the composition 2.25 CaO, 0.2 to 1.0 Cr_2O_3, 1.0 SiO_2, .2 to 1.0 SnO_2. The stains were added to glaze D4, of group B, so as to bring in .118 equiv. of SnO_2. The glazes were applied to biscuit wall tile and burned to cone 8.

Stain No. 13 produced a good clear deep red color. None of the others gave results as good as had been obtained previously.

DISCUSSION

Mr. Silverman: This point of color change was illustrated in a glass I exhibited before the Society last year and is a property of some chromium compounds, known as dichroism. If the glass is examined in single layers, it is green; if in double thickness, red: in other words, the color in that particular specimen is dependent on thickness. The same thing is true in certain chromium solutions in the laboratory. Under proper conditions

you can get either green or red or a transition from one to the other. By evaporating green chromic chloride one obtains a solution which transmits purple light if held in front of a tungsten lamp. Further evaporation produces a solution which transmits blood-red light. The greater the concentration, the darker the light transmitted. The color therefore depends either on concentration or thickness or both. If you want to see a dichroic effect for yourself, all you have to do is add a green chromic chloride solution to a red chromic nitrate solution. On looking at a lamp filament through the solution and moving the bottle from side to side, you will find that the filament is both red and green. Certain chromium compounds have this tendency.

Mr. Burt: I remember in the laboratory in Berlin, we were working on the reduction of copper and simply took a little crucible and made up a copper green glaze and then dropped into it iron filings. The iron filings reduced the copper, giving a very fine red copper, reduced there. We took that red, chipped it off, ground it up in water and then put it into a glass as coloring matter, and I was bewildered by the result. It gave exactly the effect you speak of. If you held the colored glass up and looked at it, it was red, if you looked through it it was blue. It was the same sort of thing you are speaking of; I think it is the property of light, one being the reflected light and the other the transmitted light.

Prof. Parmelee: We know that chromic acid may be a base or an acid, and that we have the coral red glazes which are made as strongly basic lead compounds, in which the chromium acts as an acid. On the other hand, we have glazes in which the chromium acts as a base and the color of the glaze is green. I have seen cases in which glazes containing chromium and much lead will show green spots and red spots, but would you refer to such as examples of dichroism?

Mr. Silverman: I do not know that I can explain this particular condition, but in the two salts, chloride and nitrate, chromium is the base in both cases, and yet you have green in one and red in the other. The appearance of red or green is not necessarily due to the position of the chromium in the compound.

EXPERIENCES IN MENDING KILN FURNITURE

BY SAMUEL RUSOFF

The mending of kiln furniture, that is, saggers, sagger lids, bats, rings, etc., is not a new scheme, but has never proven profitable with such individual materials as have been used.

The purpose of a mending material should be first to hold the broken ends together when it is freshly applied, and next, to have sufficient strength to unite the ends so that they should be able to stand fire under a strain without pulling apart at the seam.

Sodium silicate has often been used but has never proven successful when used alone. It swells at a low heat and forms a weak, honey-combed structure at higher temperatures but it has one good feature, in that it makes a good binder for cementing objects together.

Plastic clays have often been tried alone, but they lack that initial strength that is so apparent in the use of sodium silicate. Slip, ball and fire clays have been experimented with, but these have never given desired results, though possessing certain qualities that ought not to be neglected. Slip clay, although fairly plastic, lacks the initial bond, but at about cone 2 it fuses and has a tendency to run and form a compact glass between the broken ends. Ball clay of the type tested vitrified at cone 10 down, but its shrinkage prevents a gripping bond and thus serves no purpose. This is likewise true of plastic fire clay.

A combination of sodium silicate and clay either slip, ball or fire, has also been tried but has never proven really successful, because sufficient allowance had not been made for shrinkage and expansion. To offset this weakness, a waste material was introduced that was obtained from the siding department of a grinding wheel concern where the wheels were finished off. This waste material consisted of abrasive grains and some clay bond, and had a shrinkage which was almost nil. The following formula was evolved after some experimental work and gave excellent results in the mending of bats and rings at cone 11 down:

	percent
Waste material	55
Slip clay	5
Fire clay or ball clay	20
Sodium silicate (J brand 42 percent H_2O)	20

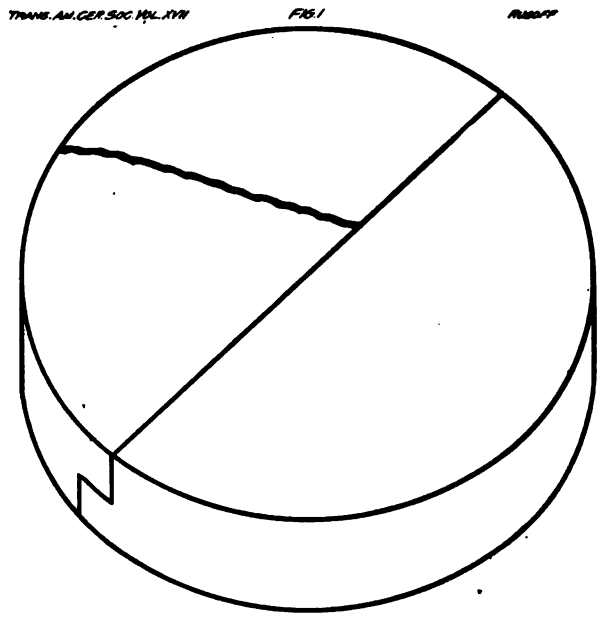
Before adding the sodium silicate to the mixture of clays and waste material, it was diluted to 38° Beaume. The thin paste produced was then easily applied with a small blade.

In the early experiments with these mixtures, very little success was realized with heavy bats. We found that small, thin bats could readily be cemented and would hold well. When we tried to apply the paste to bats 18 inches or larger in diameter, our trouble began.

The mixture was applied to each side of the break, the bat then laid perfectly horizontal, and the edges forced together. A day or two later, the seam was examined and appeared perfectly solid, but on trying to lift the bat, the pieces readily fell apart. Although a good hard crust had formed on the outside, no such condition existed on the inside of the seam. Another trial was made, but this time the pieces of the bat were tied together, and the bat was allowed to dry for a few days longer. This one also fell apart and showed similar aspects as were noted before. It was then quite apparent, that ordinary kiln room drying was insufficient to produce results in a few days' time. At a later date, some bats were mended and placed in the drier, the temperature of which was 110°F. Instead of laying the bats horizontal, they were set up vertical so that one piece of each bat rested on the lower piece, a slight pressure being thus produced. The following day the bats were examined, and the pieces seemed to hold together very firmly, but with rough handling some of them broke before being placed in the kilns for use.

In the manufacture of grinding wheels, a temperature of about 500°F. is necessary to produce the best grade of wheels by the silicate process. With this fact in mind, an oven, as used for silicate wheels, was filled with mended bats and placed so that the heel of each bat butted against an iron rod and held the bat vertical. About 80 bats, or rather half bats, were placed in this

oven, and the temperature run up to 500°F. within four to six hours. The gas was then turned off, and the oven was allowed to cool gradually. The following day, the bats were taken out, and even with very rough handling, their behavior showed that the first stage of bat mending had been successfully accomplished. On testing these mended bats in the kiln, the results proved to us that it was well worth the time and trouble, and furthermore, their repair would be an item in the reduction of the cost of our kiln furniture.



From Fig. 1, you see that the bats are made in half sections with a ship-lap joint. It is apparent, that even if one section should be broken, it could be used again as the top section, but naturally it would not be as strong, as if it were whole. If a strain were put on it, the pressure would not be equally distributed, and there would be a tendency to break the lower section, which then would cause the breaking or warping of the wheel on this bat. Further damage to wheels in upper portions

of the stand might also ensue. The mending of the upper bat prevented the unequal distribution of the strain and loss of wheels in the kiln.

The cost of the mending process figured as follows:

Mending mixture, 40 pounds at 1 cent	$0.40
Labor, 3 hours at 20 cents	.60
Gas	.65

Number of bats mended, 80; cost per bat or section, 2 cents. Original cost of bat, probably 25 cents or more.

This represents a small item in comparison with the original cost of the bat and readily shows the value in mending bats for re-use.

The use of waste material as given above is not absolutely essential, and where such material is not available, a fine grog 40-60 mesh could be substituted. By making a few tests, old glaze material could be substituted for the slip clay. The cost of slip clay is small and naturally would not necessitate such a change unless there were large quantities of waste glaze on hand. To obtain the best results from the mending mixture, heat treatment should be considered, and adjustment of the clay contents should be made if mixture is to be used at other than cone 11 down.

DRILLING AND BLASTING SHALE BANKS

BY D. E. HUMPHREY

The selection of the proper blast hole drill furnishes a problem for each shale bank. The blasting qualities of the shale, the height of the bank, and the method of loading and hauling to be used should be taken into consideration. During the last few years we have had considerable experience with a number of different types of blast-hole drills. At present, we use five different types of drills, each possessing peculiar advantages in the particular character of work in which they are used.

FIG. 1

The old hand drill (Fig. 1), consisting of a steel drill threaded to a ¾ inch pipe handle, will always be of service for small jobs where it is difficult to supply air or steam. This type of drill is adapted to small holes and to depths not to exceed fifteen feet. It is preferable to the steel and sledge in soft materials such as shale where only slight blows are required to do the cutting. The cuttings are easily cleaned from the hole with a long handled auger.

A thread bar auger drill, of the type generally used in clay and coal mining, will drill horizontal holes in soft dry shales.

We have successfully brought down a 30 foot bank by drilling 12 to 15 foot holes with a hand drill at the top of the bank, and 15 to 18 foot horizontal holes at the bottom with a thread bar auger drill and firing electrically both top and bottom holes at the same time.

FIG. 2

The compressed air hammer rotating drill (Fig. 2) will drill small holes in a dry bank faster than any other drill I have ever seen. Where the conditions were good, I have seen a four foot hole drilled in less than four minutes. Part of the exhaust from these little machines can be turned down through the hollow drill

to blow the cuttings from the hole. Ordinarily 1½ inch holes and 6 foot depths are the limits of the smaller size hammer rotating drills. For best results, these drills require about 50 feet of free air per minute, under a pressure of 80 to 100 pounds. Rotating hammer drills are especially valuable where there are many large pieces to be broken. Adobe blasting or mud capping is

FIG. 3

wasteful from the standpoint of the use of explosive. Much less dynamite will give better results if well stemmed in the bottom of a small hole drilled to the center of the piece to be broken.

Steam or air tripod drills are adapted to vertical or horizontal holes up to four inches in diameter (Fig. 3). Depths greater than 20 feet can be reached, but the long steels required for deep holes are difficult to handle. Under good conditions, this type of

drill will make 60 to 90 feet of vertical hole and 20 to 50 feet of horizontal hole per day.

The secret of fast drilling in shale is to dress the drills to the shape of a blunt chisel about one-quarter inch wide, instead of drawing them out to a sharp cutting edge. The blows from

FIG. 4

the blunt chisel drill will reduce the size of the cuttings so they may be washed out of the hole, as fast as the drill progresses, by a jet of water from a small pipe fed down to the bottom of the hole. For rough ground, which will not permit the use of a well drill, or for ledge blasting the tripod drill may be found very satisfactory.

The well hole type of drill (Fig. 4) has a decided advantage

over the tripod drill because it is a complete unit in itself. It is not necessarily dependent on a supply of steam or air from the power house. We at first tried out the large diameter blast hole in a small way. An old type spring-pole well drill was erected (Fig. 5) and a couple of five inch blast holes drilled. The big holes were so satisfactory that we purchased a gasoline driven horse drawn drill for one factory and a traction gasoline driven machine for another plant, where the number of moves and set-ups made the traction machine more desirable.

FIG. 5

The average capacity of a well drill in shale is 70 to 80 ft. per day in good drilling. Forty feet per day is considered good service in limestone. We have found that it pays to use a well drill for holes as shallow as eight feet, if the ground be level enough to move from hole to hole without taking down the tower.

During the last few years there has been a tendency toward large diameter blast holes. It is generally believed that the explosive action is more complete and instantaneous in large diameter holes. The amount of explosive per lineal foot of hole is

greatly increased in larger holes. It varies as the square of the diameter of the hole.

In locating blast holes one must depend principally on common sense and experience. There are, however, a few general rules for locating holes which may be of value to the man who is trying big blast holes for the first time. It is generally safe to place the hole one-third to one-half of its depth back from the breast or face of the bank, provided this does not exceed 25 feet.

FIG. 6

The distance from center to center of holes should be one-fourth to one-third of the depth. The amount of stemming should not be less than one-third of the depth of the hole. One pound of dynamite in easily blasted material will bring down four tons of shale. When the face of the bank is not perpendicular, and there is considerable of a toe at the bottom, it is a good plan to spring the bottom of the hole with a small charge, so that a larger pro-

portion of the charge can be located behind the greatest resistance. Blast holes can be located a greater distance from the face of the bank, if the material shatters easily from the shock of the explosion. In case the material does not shatter easily, and there are too many large pieces, the holes should be placed closer to the face and nearer together . This may necessitate drilling a smaller diameter hole to avoid too large a charge in one hole, and to make the explosive fill the hole to the proper height. Material for stemming should have the property of absorbing a shock without being blown out of the hole. The best material for this purpose is dry ground shale as it comes from the dry pan, or well tamped sand.

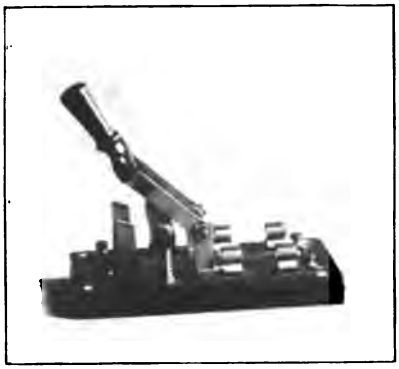


FIG. 7

It is a good plan to fire several blast holes at once. More material will be torn down per pound of dynamite, and the cross forces from the different holes will break the shale into smaller pieces.

Blasts should be fired by electricity except where single charges are exploded. The ordinary magneto blasting battery with the caps connected in a series is not so satisfactory as a line from the lighting system, to which the caps are connected in parallel. Blasting caps sometimes have bridges of unequal strength. When the caps are connected in series the caps which have the highest resistance in the bridges are apt to explode before the caps with the low resistance bridges get enough electricity to ex-

plode them. This is apt to be the cause of mis-fires in part of the holes. We have secured the most satisfactory results by connecting the caps in parallel to an ample supply of electricity from the generator. By this method the mis-fire from unequal resistance in the bridges is entirely eliminated.

I have not been able to determine how much electricity is required to explode a cap. The resistance in a cap is about the same as the resistance in a 16 candle power carbon filament lamp. The switch board ammeter scarcely makes a tremor when 30 to 50 caps, connected in parallel, are exploded. The ordinary am-

FIG. 8

meter is perhaps too sluggish to indicate such an instantaneous flow of current. We have found it ample to fuse the blasting circuit with an allowance of one-half ampere to the cap on 110 volt circuits. To avoid the danger of connecting caps to live wires, the blasting circuit should be equipped with a spring switch which breaks the contact as soon as the handle is released, (Fig. 5).

When there are 500 pounds of dynamite in the hole, which at 12 cents a pound is worth $60.00 it is a poor plan to economize on blasting caps which cost but a few cents each.

The United States Bureau of Mines, in *Bulletin No. 59,* states that a No. 6 cap, which contains one grain of mercury fulminate will produce 10.4 percent more explosive force in the dynamite than a No. 5 cap, containing three-fourths of a grain of mercury fulminate; and that a No. 8 cap, containing two grains of mercury fulminate, will produce 14.9 percent more explosive force in the dynamite than a No. 5 cap. This means a considerable saving in explosive when No. 8 caps are used.

My experience leads me to believe that better detonation in large charges of explosive is secured by the use of a cap near the bottom, one in the middle and one near the top of the charge. Even if the cap tests all right it is much safer to use more than one. Sometimes a wire is broken in tamping the stemming. If two caps have been used, the charge can still be fired. It is an unpleasant situation for the steam shovel operator, when one of the holes mis-fire. A charge of dynamite containing and unexploded cap is a delicate thing to handle with a steam shovel or to grind in a dry pan.

When two or more caps are used in a hole, there is danger of connecting the two wires from one cap to the same lead wire from the supply of electricity. An easy way to avoid this is to have the caps made with two differently colored wires. That is, one of the wires might have red insulation and the other might have white insulation. In connecting caps to the lead wires, all the red colored wires should be connected to one lead and all the white colored wires to the other. It is well worth while to purchase a cap tester and to test each cap both before it is placed in the hole, and again when the connections are made to the lead wires. There are several makes of cap testing galvanometers on the market, made for this particular use. When testing with the galvanometer a very small current passed through the cap. If the galvanometer is properly constructed, the amount of current is so small that there is no danger of causing an explosion.

The kind of explosive which is best adapted to a shale bank can only be determined by careful comparative trial. Straight nitro-glycerine dynamite is apt to be too fast for shale.

Ammonia dynamite generally gives better results than

FIG. 9

straight dynamites, but it deteriorates in water and may give trouble in wet holes.

Potassium chlorate dynamite seems to give good results in shales, but it is not widely used.

Nitro starch dynamite is non-freezing and does excellent work in shale.

Blasting powder is one of the cheapest explosives but it is, of course, not suitable except in very dry holes.

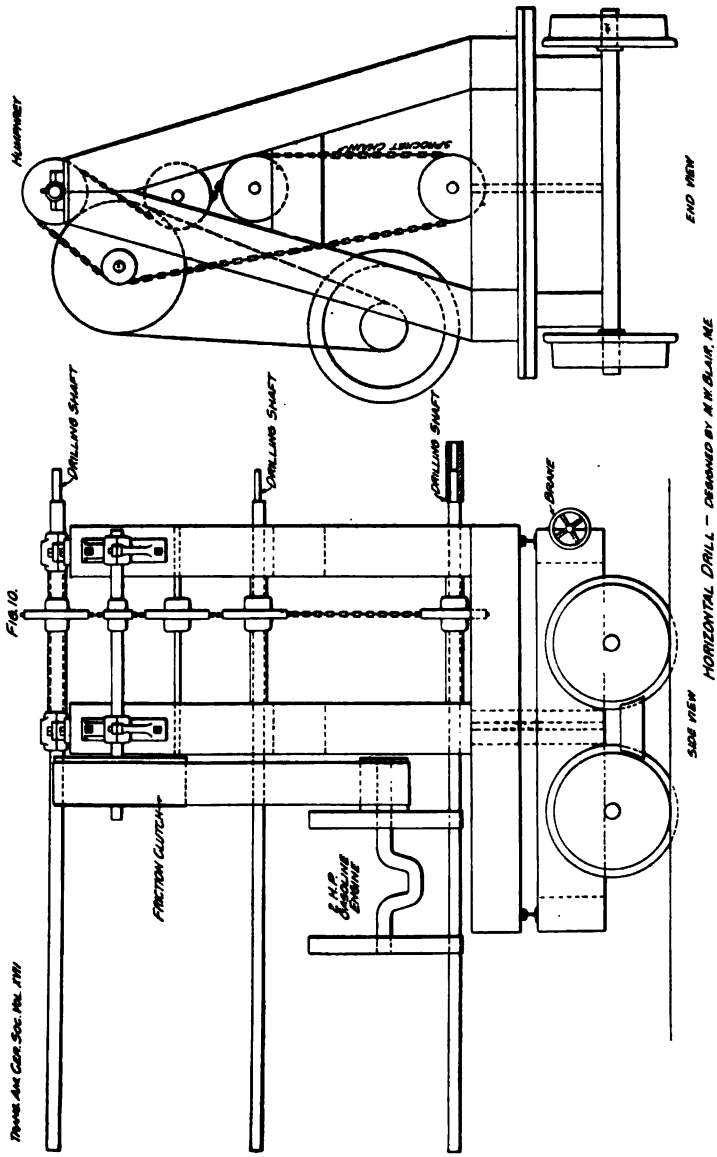
We have used all five types of explosive and find the nitro starch very satisfactory for big blasting, particularly in cold weather.

The thawing of a ton or two of dynamite is a difficult problem unless a large and expensive thaw house is available.

There are two reasons why big blasting and large blast holes are more efficient. The principal reason, of course, is that large amounts of explosive properly loaded and fired will bring down more tons of shale than if fired in several small blasts. The second reason is that the money involved in big blasting justifies the attention of men of a higher grade of intelligence and ability than is ordinarily found in the pit boss who daily drills a hole and with a few sticks of dynamite blows down enough shale for the next day.

DISCUSSION

Mr. Blair: This paper is of interest to me. I have had some little connection with, and experience in dynamiting shale, using nearly a ton of dynamite a month for that purpose. I would like to add a drill driven by a gasoline engine to those Mr. Humphrey enumerated a horizontal screw feed, thread bar drill, with power applied to the drills. A gasoline engine furnishes the power in places and on plants which are devoid of electrical power or air compressors. The air compressor usually involves a little larger investment than a small plant cares to put into that sort of equipment, and a great many plants, especially in the natural gas region, have never felt the necessity of putting in electrical equipment. They use natural gas very largely for light and hence do not feel the need of electrical equipment. The


HORIZONTAL DRILL - DESIGNED BY H.W. BLAIR, ME
END VIEW
SIDE VIEW
HAMMER
SHOCKAT CHAIN
DRILLING SHAFT
DRILLING SHAFT
DRILLING SHAFT
BRAKE
FRICTION CLUTCH
4 H.P. GASOLINE ENGINE
TRANS. AM. GEOL. SOC. VOL. XVII
FIG. 10.

adaptation of gasoline power to a drill for mine work is very economical, especially where the work is hard to reach, and where the water makes the use of the electric current rather dangerous. I have built a drill for that purpose using that type of power, and it will drill a foot a minute, in an excessively hard shale. Two men operate the drill, and a two horse gasoline engine drives it. It can drill an inch and three-quarter hole, 12 feet deep, and it is adaptable also to the open shale bank, drilling holes at the bottom of the drift. Inside the mine I am able to reach as much as a 12 by 14 or 14 by 14 face, drilling twelve to fourteen holes in that face, and drilling an open point in the face.

If you will permit me, I will give you a rough sketch of the way that drill works in the mine. Here is the roof, here is the floor; here is the face to be drilled. We have the ordinary coal mine jack through which a thread bar attaches here to the auger drill. This jack is tightened top and bottom in the mine. Say the vein there is 12 or 14 feet deep. By a universal joint or two universal joints at this point, I connect the thread bar to a shaft which is key-seated and fed forward just as the upright shaft is fed on a key seat in a drill press. The power is applied from a friction clutch to a drive shaft and a sprocket chain. The key-seated shaft feeds through a sleeve with the key fastened in the sprocket. The power can be thrown on and off by the friction clutch. (Fig. 10.) A gasoline engine sits back on the end of the truck. By having a series of these sprockets, all driven by the same chain, running over one sprocket, behind one and over the other, you can get as many as three different levels for that feed shaft and by that means can drill a hole at 6, 8 or 10 feet above the floor of the mine. I found that machine very effective and very economical. It was inexpensive to build, I think it cost less than one hundred dollars to build the machine. Two men operate it and can drill a foot a minute, an inch and three-quarter hole, in what we consider a very hard shale. Now, that is for mine work. For use in the open pit, we simply use the same machine and instead of the mine jack, the lock nut through which the thread bar is fed, is fastened and braced back to the machine so that the weight of the machine, which is rather heavy,

is against the drill; it probably weighs a ton altogether. It has a very heavy wooden frame but is quite easily moved; if on a track, the machine can be pushed along the track by one man. The bed of the machine has a swivel base so that you can get any horizontal position you need.

Mr. Richardson: How many revolutions does the drill make?

Mr. Blair: About 85 revolutions a minute. The gasoline engine runs about 300 a minute.

Mr. Hice: Will the State Mining Department permit the use of a gasoline engine in a mine?

Mr. Blair: They never have questioned that. In Pennsylvania a mine employing less than 15 men has never been subject to State inspection up to the present time. They may effect something of that kind; legislation is getting pretty severe on that subject.

Mr. Humphrey: At present the Pennsylvania laws permit the use of gasoline engines in a mine. The Ohio mine laws do not. Of course in a strictly shale mine there is no explosive dust which would make dangerous the use of gasoline in a mine. I think possibly that is the reason it has never come under State inspection in that particular.

Prof. Parmelee: I hope that Mr. Blair will furnish sketches to go with this discussion in the Transactions.

Mr. Blair: I will.

Mr. Smith: We have had some experience in blasting shale, but have never used any drill machine. In order to get the required amount of ammunition in the bottom of the hole, we would, after drilling the hole, explode some light charge of dynamite so as to pot it, as we call it, and in that way we get what Mr. Humphrey does in the large hole without any special machinery for making such a large hole. Our experience is that it pots it sufficiently. Then we use black powder, and we make pot enough so that we can get enough of this black powder in the bottom of the hole. Our stuff is harder in the bottom than in the top. We have obtained very good results by that method. Mr. Humphrey said that when he exploded single holes—he didn't

say he wouldn't use electricity, but advised electricity all except for single holes. Why not use electricity for a single hole?

Mr. Humphrey: When more than one hole is exploded at a time, electricity should always be used. Where one small charge, located in a difficult place, is to be exploded, it is often more advisable to use a cap and fuse than it is to carry around a blasting battery and arrange long load wires.

Mr. Smith: My opinion would be that it is more advisable to use electricity even in the one hole, for the reason, that a fuse is not nearly so reliable, the time is longer, and a fuse has been known to hang fire. When you attempt to explode the electric cap, and it does not explode, you do what you want to do, knowing it will not explode, but if the fuse don't explode, you don't know whether it has gone out or is hanging fire.

Mr. Humphrey: I agree that electrical blasting is better and gives better results. We merely use the fuse and cap because it is convenient when going down over a large hill, for instance in that last picture of a blast, there might be half a dozen chunks from the blast that would need pot shooting, as we call it, and then we prefer to use a fuse and cap.

Mr. Blair: I have found the use of electrical exploders to be very satisfactory in outside work such as Mr. Humphrey refers to. In a mine, however, you often have conditions of propping which makes the putting off of six or eight blast holes at one time undesirable, especially where you have to carry your props up to the face. Such practice would be quite expensive for the reason that, when you blow out a chunk of shale 12 or 14 feet square, and down a mine entry, the props generally go, and it costs considerable money to replace them. We have found it very satisfactory on a face of that kind, to drill say three holes in the center, four or five in the middle and three on the top, then to spring one center hole. Put into that center hole one or two sticks of dynamite, explode the charge, and then load that hole rather heavily as compared with the other holes. It usually requires in our materials six or eight sticks to the hole, and in loading the center hole, twelve or fifteen sticks or six or eight pounds of dynamite. These holes are 7 or 8 feet deep. We cut

our fuses in such lengths that the heavy hole will be fired first, and the springing of that hole and the extra quantity of dynamite gives you an opening there which will then allow the timing of the proper holes in rotation, blowing your material to the center of the shot or the center of the room and not down the entry, and we have found that to be of considerable advantage.

Mr. Richardson: I am very glad that we have this paper in our records. Mr. Humphrey has taken up a subject that is of general interest to brick manufacturers. In regard to power drilling and shooting—we are in a mining country, a coal mining country, and the clay miners were formerly coal miners or they are descendants of coal miners, and there is a great deal of practical information among those people about the drilling of holes and the shooting of powder and dynamite. As this work is all done by the ton, and they pay for their own powder, we leave it to them, but it is quite noticeable, the difference between some of the old expert miners and the younger men in the amount of powder used. We don't have to dictate in regard to where they drill their holes, nor how they fire them, because they are doing the work by the ton, so I have not given that point very much study. I will say, however, that the electric auger drilling machine is used in many clay mines of the Hocking Valley. I don't believe that we would be permitted to use a gasoline engine in our mines, not that there are any explosive gases in clay mines, but we are under very rigid inspection in Ohio and especially throughout our district, and anything that even made bad air in the mine would be objectionable and probably would not be allowed. They won't let us use dynamite because of its unhealthful action on the men in the mine, and electric power or compressed air is the only practical thing for us. Pretty good drills of the type Mr. Blair has spoken of, using electric power, are now on the market. Electrical power is usually more practical because it can be used for haulage and for so many purposes about such a plant.

DEVELOPMENT OF SHIVERING IN A FIRE-CLAY BODY

BY R. H. MINTON

In the course of many experiments conducted upon a great variety of New Jersey clays with a view to determining their suitability for use in a fire clay body, such as is used in the manufacture of architectural terra cotta and similar ware, the interesting and constantly recurring question has often presented itself as to why a certain slip and glaze would craze badly on one clay and at the same time shiver badly on another.

Aside from the question of the adaptability of a particular slip and glaze to a clay, or body, there are certain clays that show a very strong tendency to cause crazing, with a slip and glaze combination of almost any type that can be applied to them. There are clays also that seem to defy the application of a slip and glaze—the clay causing these to peel off in large patches, unless artificial means are taken to overcome it.

In the production of a body from natural clays it is good practice to test each clay individually first in the raw state, then making it up into a body, so that its characteristics may be learned in drying, in burning and after firing.

It is easier, by manipulation of the slip and the glaze, to overcome crazing in a fire clay body than to overcome shivering or peeling. Therefore, a certain balance must be maintained between the clays of the different types in order to produce a body as safe as possible.

Clay Types. There are two New Jersey clays that beautifully illustrate the extremes of these two types of clays, and these are used in large quantities in the production of widely different kinds of clay wares.

Clay "A" is a very close grained, fat clay, with high plasticity. One hundred pounds carefully selected from a carload, blunged to a slip and put through an 80 mesh sieve showed absolutely no sandy residue, nor any other kind except a few ounces of black iron pyrites. At cone 8 this clay is vitreous, showing a

shrinkage of 1½ in. to the foot from the natural state. Almost any slip and glaze on this clay alone will craze badly.

Clay "B" is more of a fire clay, although its stickiness, plasticity and bonding power seem to be fully equal to clay "A." This clay shows a shrinkage of slightly less than one-half of that of clay "A," and, while dense and hard, shows no indication of vitrification. One hundred pounds of this clay put through an 80 mesh sieve shows about one and one-half pounds of sandy residue, and no doubt much more passes this mesh.

This clay alone, or when made into a body with grog, will shiver any slip and glaze that ever has been applied.

FIG. 1

The total soluble salts in clay "A" amount to 0.50 percent, that in clay "B" to 0.075 percent.

Clay "A" is quite rusty and probably contains considerable sulfate of iron.

A comparison of these two clays brought out the question: whether clay "A" could not be made to develop shivering in a slip and glaze (that crazes on clay "A" alone) by the introduction of a foreign element. Among the suitable substances that might bring this about are flint, sand, ground fire brick and soluble salts.

For this series flint was selected as the most promising, and the following series of bodies was made up:

Body No. 43—Clay "A" two parts, to 16-mesh sagger grog one part, by weight.
Body No. 44—to body No. 43 add 5 percent by weight of flint.
Body No. 45—to body No. 43 add 10 percent by weight of flint.
Body No. 46—to body No. 43 add 15 percent by weight of flint.
Body No. 47—to body No. 43 add 20 percent by weight of flint.
Body No. 48—to body No. 43 add 30 percent by weight of flint.
Body No. 49—to body No. 43 add 40 percent by weight of flint.
Body No. 50—to body No. 43 add 50 percent by weight of flint.

About ten pounds of each body was carefully made up with sufficient water to press well, and after standing for five days, covered with wet bags, was pressed into tiles 4½ in. by 3 in. by ¾ in.

When thoroughly dry, all the bodies were coated with a slip and a glaze that have proven capable of fitting all practical bodies to which they had been applied. Both the slip and the glaze were first made into a stiff jelly with glue and applied with a brush, six coats of slip and three coats of glaze.

All trials were fired at one time in a large muffle kiln reaching cone 8 in 138 hours and cooling in 144 hours.

The results, which are clearly shown in Fig. 1, are as follows:

Body No. 43—No crazing or shivering. Glaze fits perfectly.
Body No. 44—Slight shivering on the corners only.
Body No. 45—Some shivering on both corners and edges.
Body No. 46—Strong shivering on both corners and edges.
Body No. 47—Very bad shivering all around edges. Large patches flaked off.

Body No. 48—Slightly worse than body No. 47. Body on edges torn away.

Body No. 49 and No. 50—Somewhat larger area flaked off than on body No. 48.

Introduction of flint into a fire-clay body has produced shivering of a most pronounced form in a well fitting slip and glaze.

In this instance, with a clay which alone (without grog) will craze badly, five percent of flint is sufficient to start shivering,

and the results are increasingly demonstrated with additions up to 40 percent.

Conclusions: Here we seem to have a definite solution of the question that started the animated discussion in Volume IX, pages 520 to 527, as to the production of shivering in a terra-cotta body by the soluble sulfates introduced by the fire brick grog.

In that case, the suspected grog contained 1.36 percent of SO_3. The writer knows from experience that a body, in which there are more than fifty percent of the clays by weight and containing high percentage of soluble salts, will very often cause shivering or flaking of slip and glaze, unless means are taken to counteract it. But to maintain that the introduction of even 30 percent of fire brick grog containing 3.36 percent SO_3 will cause shivering for this reason, seems untenable, especially when the body was treated with barytes.

The highest grades of fire brick made in New Jersey contain little or no grog from burned clay, but their non-plastic is a silicious material known locally as "spar"—and many attempts to substitute crushed fire brick for crushed saggers as grow in a fire-clay body have demonstrated that the havoc wrought by the fire-brick grog is not due to soluble salts, but to the silicious matter they contain.

TIME TEMPERATURE CURVES DURING SALTING OF SOME OIL-FIRED SEWER-PIPE KILNS

BY F. H. RIDDLE AND A. L. GLADDING

The salting of sewer pipe, no matter where or under what conditions, seems to be accompanied with more or less uncertainty. Two of the essentials for successful salting are sufficient heat to volatilize the salt when the ware is properly burned, and the proper draft. Both are equally important. If the ware being salted is slow to take the glaze, as is the cast of most No. 2 fire clay bodies, the problem of maintaining the proper temperature in the fire boxes sometimes becomes troublesome. The vaporizing of salt is an endothermic reaction, and the general belief seems to be that the loss of heat, after continued salting, is due to this reaction alone.

A customary procedure in salting is the use of a reducing atmosphere. There seems to be various opinions as to the necessity of this. Regardless of whether or not this is a benefit from a chemical standpoint, it is of assistance from a commercial standpoint, more especially with a light burning or buff colored body. A pipe having a thick glaze will sell regardless of color, while with a thin glaze or a flash, it will not sell. The darker the color, the more nearly the piece will look like the better glazed ware. Therefore the more reduction the better, so long as the body is not smoked until weakened, as can easily be done with some clays.

Where the glazing requires considerable time, as in the case under study, the maintaining of the salting temperature is of considerable importance. Where coal is the fuel, and the firing is intermittent, the problem is more difficult than where oil is used, since the oil can be fed continuously regardless of the salting. In overcoming this loss of heat, the question to consider is, what causes it? Is it entirely due to the salting, or are there other causes? The writers believe that there are other causes, as well as the salting, at least in the case under discussion in these notes.

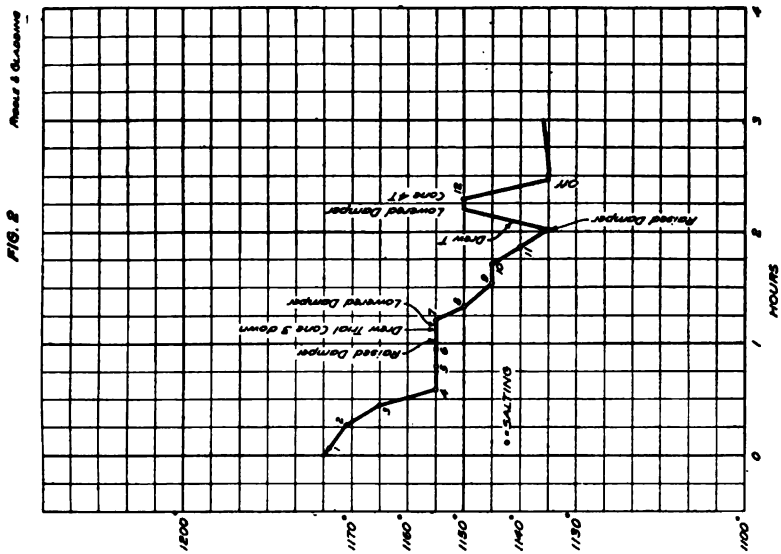


FIG. 2
Raised Damper
Lowered Damper
Drew Trial Cone 3 down
Raised Damper
Lowered Damper
Drew T
Raised Damper
Lowered Damper
Cone 4 T
Off
• = SALTING
HOURS
1200°
1170°
1160°
1150°
1140°
1130°
1100°

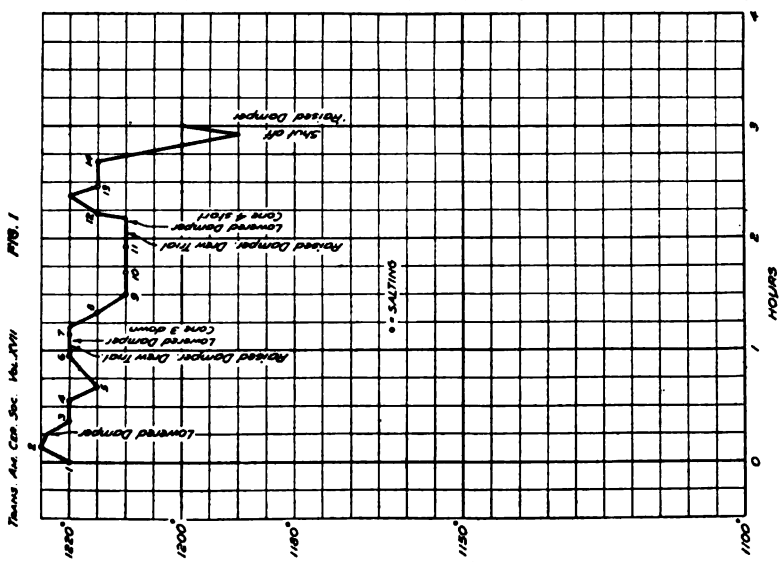


FIG. 1
Lowered Damper
Raised Damper. Drew Trial
Lowered Damper
Cone 3 down
Raised Damper. Drew Trial
Lowered Damper
Cone 4 start
Shut off
Raised Damper
• = SALTING
HOURS
1220°
1200°
1180°
1150°
1100°

A brief description of the local conditions will be of assistance in studying the accompanying figures. The kilns are the ordinary type of round, down-draft kilns with checkered floors. The bottoms have a center well hole, with radial flues leading out to points at the side wall midway between the bags. Each of these radial flues has three properly spaced inlets to take the gases from the feather flues above. The inside diameters of the kilns are thirty and thirty-six feet. Both sizes salt equally well. The number of fire holes in each kiln varies, there being ten or twelve, depending on the diameter. The fire holes are 20 inches to 24 inches wide and from 3 to 4 feet high. None of these variations seem to affect the working conditions to a noticeable extent.

The fuel oil, which is commonly used in California, contains about 18,500 B. T. U., and is supplied to the kilns under pressure. This pressure is of little consequence, so long as it is constant, and great enough to furnish the volume required. The atomizing agent is air, at a pressure of about 25 pounds to the square inch, at the tank. This will be considerably lower at the burners. The air pressure is of great importance, and is determined by the pressure at which the burner will atomize. The lower the pressure, the better, since the cost of compressing the air is reduced, and the action of the fire on the kiln arches will be less severe. Too low a pressure will not atomize the oil sufficiently to make good combustion, and will not raise heat fast enough. There are so many burners on the market, and so many home-made ones which apparently do equally well, that no description seems necessary. We would like to state, however, that the air and oil first come in contact with each other after they leave the tip of the burner.

The fire boxes in the kilns were arranged with the burners about eighteen inches from bottom, horizontal, and the tips flush with the face of the kiln. The fronts of the boxes were built up with a four inch wall of brick, allowing a six inch square opening around the burner, and an opening the full width of the box extending down from the top ten inches. These top openings

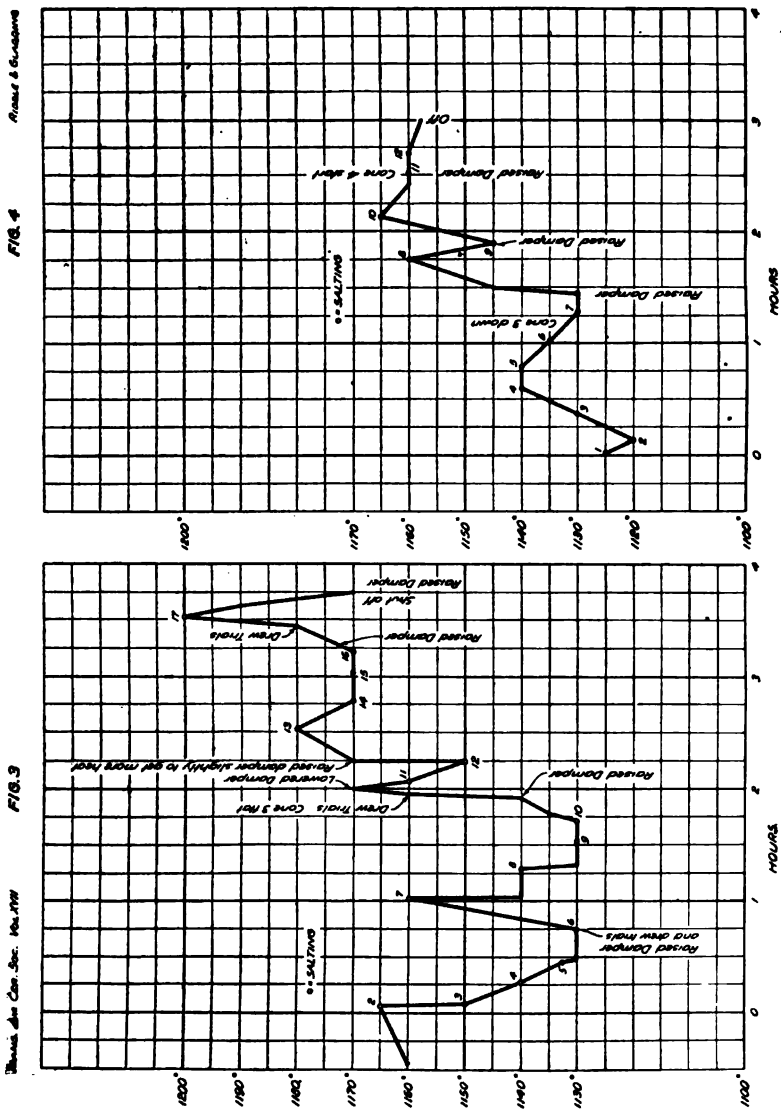


FIG. 4
Riddle & Gladding
Raised Damper
Cone 4 start
Raised Damper
Raised Damper
Cone 3 down
Off
• = SALTING
HOURS
1200°
1170°
1160°
1150°
1140°
1130°
1120°
1100°
FIG. 3
Raised Damper
Shut off
Raised Damper
Drew Trials
Raised damper slightly to get more heat
Lowered Damper
Drew Trials Cone 3 flat
Raised Damper
Raised Damper and drew trials
• = SALTING
HOURS
1200°
1190°
1180°
1170°
1160°
1150°
1140°
1130°
1100°

were filled in with loose bricks until time to salt, when they were taken out, so the salt could be thrown in.

The arrangement described above was used on all kilns but the one as shown in Fig. 4. Here a rectangular opening was used, of dimensions one brick wide (nine inches) and three bricks high (eight inches. At the center of this opening, on the bottom was a smaller opening three inches wide and four inches deep. The burner was set into this opening about an inch and as near the top as possible. The burner was eighteen inches from the bottom of the box, and the opening properly made around it. The 8 in. by 9 in. opening above the burner could be stopped by putting three bricks in it. The front was bricked up to the arch, with the exception of an opening at the top about the size of the end of a brick, which was used as an inlet for cold air to relieve the arch when too hot.

In the second case, the salting was done through the hole above the burner, the three loose bricks being removed to do this. In both cases the salting openings were left open through the salting process. At this stage, the kilns are dampered so low that there is very little chance for any cold air to get in.

The body, a No. 2 fire clay mixture, requires considerable time to take the glaze, and is considered a hard body to glaze. The usual procedure with the ware is as follows: When the proper cone has gone down (cone 2) the damper is lowered until the draft is practically balanced. This can be determined by opening the peep hole in the center of the wicket. If the draft is right, the gases and flame will lazily issue from the hole.

The salting is done at approximately twelve minute intervals, and a shovelful of salt is thrown in each box at each salting. The interval is lengthened when trials are drawn, as the damper has to be raised, and the kiln cleared up to see the cones and to draw the trials. This is done three times during the salting unless the kiln is irregular in some way. The time of salting is usually about three hours, and the kiln is salted about twelve to fourteen times during the process. The last trial is usually drawn at the end of the salting period and does not show on the figures. If the ware shows only a flash, when the

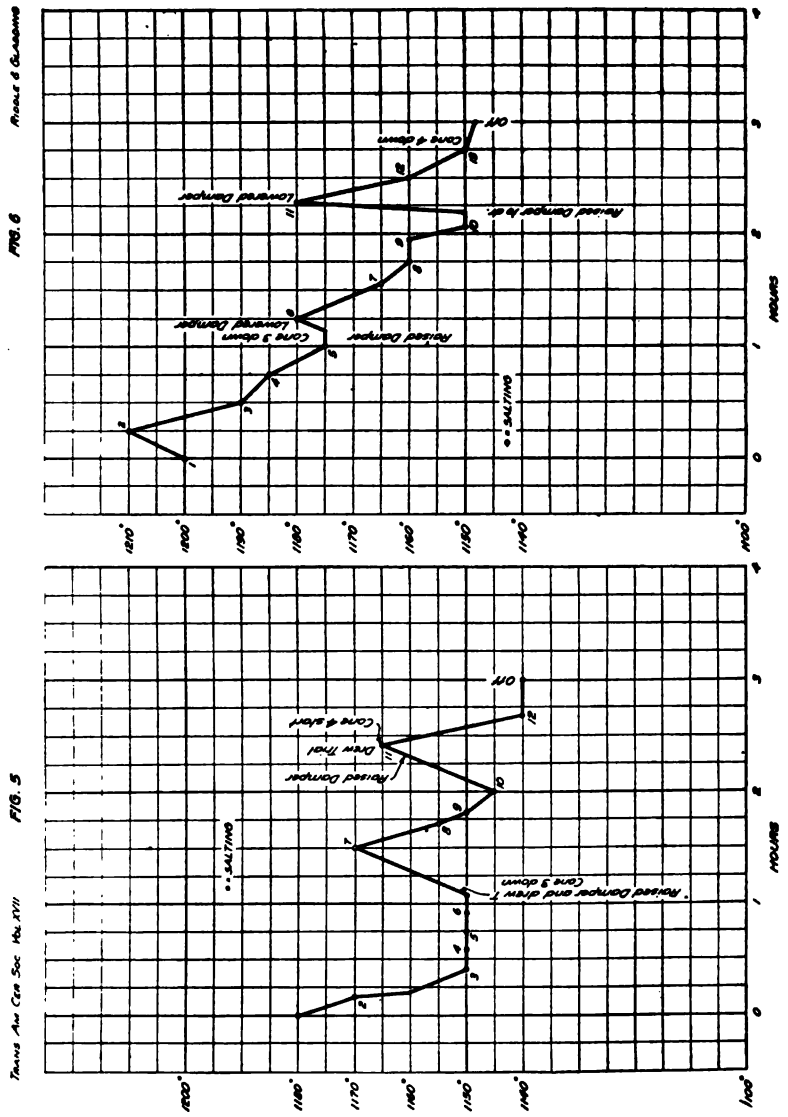


FIG. 6
Raised Damper & Cleaning
Raised Damper and drew 7 Core 3 down
Raised Damper
Core 3 down Lowered Damper
Lowered Damper
Raised Damper & dr.
Core 4 down
OFF
SALTING
HOURS
FIG. 5
Trans Am Cer Soc Vol XVIII
Raised Damper and drew 7 Core 3 down
Raised Damper
Drew Thal
Core 4 down
OFF
SALTING
HOURS

first trial is drawn, it indicates that the draft is too strong, and the damper is lowered slightly. This adjustment will usually make the glaze take hold, if the heat is right. When the salting is completed, the damper is raised, and the salt holes are left open from four to six hours to clear the kiln, and produce a bright glaze.

The accompanying figures show one curve for an entire burn, and the detail for salting on eight burns. The pyrometers used in taking the readings were the regular kiln equipment consisting of twenty-four inch platinum, platinum-rhodium thermo-couples placed about two feet away from the kiln crown hole and encased in porcelain tubes protected by an outer three inch fire clay tube. The couple projects into the kiln about four inches. The cones are placed one pipe high, near the wickets.

The chief things to note on the figures are, that in nearly every case there is a loss of heat during the salting. This varies from 50° C. to 15° C., the average loss being about 30°. Figures 3 and 4 are special cases and are not included in the determination of the average loss.

One will notice that, although there is a loss over the whole period, there are stages where very sudden rises in temperature occur. In every case but Fig. 4, these rises occur directly after the damper has been raised to clear the kiln to draw trials, and the temperature stays up until the damper is lowered again. On most of the curves you will notice that a charge of salt is put in immediately after the damper is lowered again. This makes it appear that the salting has as much to do with the subsequent loss of temperature as has the lowering of the damper, and the resulting reducing conditions due to cutting down the air supply.

The following, however, would make it appear that the lowering of the damper had more to do with the drop in temperature than had the salting. Figure 2 shows a gradual loss of heat after the second salting. Note how this decline is accelerated at the point where the damper is lowered. It might be well to mention here that, as a rule, the first two or three saltings are done before the damper is lowered to the proper point. Note

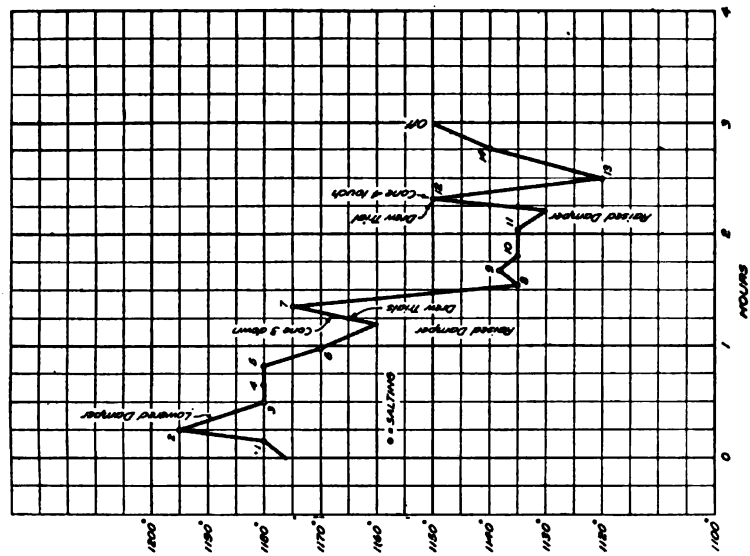

Lowered Damper
Cone 3 down
Raised Damper
Drew Trials
Drew Trial
Cone 4 touch
Raised Damper
OFF
• = SALTING
HOURS
1200°
1190°
1180°
1170°
1160°
1150°
1140°
1130°
1120°
1100°
0
1
2
3
4

FIG. 8

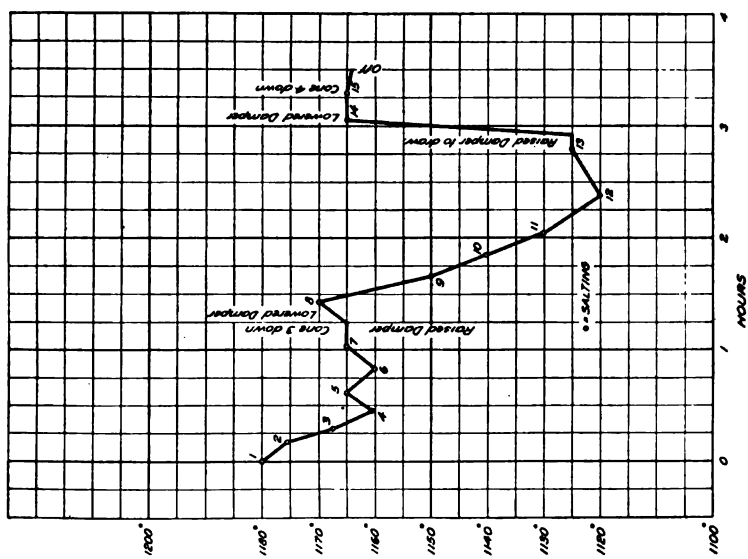

Cone 4 down
Lowered Damper
Raised Damper to draw
Lowered Damper
Cone 3 down
Raised Damper
OFF
• = SALTING
HOURS
1200°
1180°
1170°
1160°
1150°
1140°
1130°
1120°
1100°
0
1
2
3
4

FIG. 7

the effect of lowering the damper, as shown on Fig. 3, at the end of the second hour. Also note the two or three cases where salting was started before the damper was lowered, and that the heat continued to rise until the damper was lowered. See Figures 1, 6 and 8.

Figure 3 represents a burn in which there was trouble, and the ware did not take the glaze. It seemed advisable, after the second trial was taken, to raise the heat. This was done, as shown, fifteen minutes after the second hour, by raising the damper. It required extra salting to get the glaze, probably because the ware was not hot enough at the start to take the glaze properly.

Figure 4 is entirely different from any of the other curves. Here, the temperature increases from the beginning to the end of the salting, and in several cases, immediately after the salting. The reason for this is the change in fire box fronts, as previously described. The boxes were arranged with smaller salting holes and lower down in the fire box fronts. The results of this change warrants a further study under the same conditions. It is hoped that the results of these continued experiments can be described later.

The general conclusions to be drawn from the experiments so far obtained are not definite. The indications are that the reducing conditions have as much effect as the salt, or even more, in causing fall in temperature. The reducing conditions are caused by the lowering of the damper and the resulting decrease in air supply.

It is hoped that discussion from those interested will cover the following points, viz.:

First, the effect on salt glaze (brightness of glaze, causes, etc.) of rapid cooling directly after finishing, the cooling not being continued to a point where the pipe are in danger. Second, crude oil burners. The effect and advisability of mixing the oil and atomizing agent after leaving the tip, as compared with the mixing in the burner.

NOTES ON THE MANUFACTURE OF PLASTER MOLDS

BY GEORGE A. WILLIAMS

In searching the literature, one is surprised to find to how small an extent plaster of Paris, plaster molds and mold-making are treated. Very little work has been done on these subjects; and writers, either intentionally or otherwise, give only the vaguest reference to the different methods employed to attain certain desired results.

Great quantities of plaster are used each year. For example, in England in the year 1904, between 30,000 and 40,000 tons were used in making pottery molds alone.[1] We can be certain that this amount has not fallen away since that date. The greater part of this plaster is discarded after some time because of wear or breakage, and represents almost a total loss as little of this is recovered, and that recovered is of doubtful value. So one can see that the item of plaster and mold making might be the difference between prosperity or failure in a large pottery plant.

As plaster of Paris is the only substance from which pottery molds are made, the potter has for a long time tried to introduce other ingredients into his plaster, which will make it stronger and less liable to break or wear out, and yet retain all the porosity possible, in order that the capacity of each mold be kept as high as possible.

Breakage can be checked by two methods: first, care in handling and drying the molds; second, getting the strongest possible mold when the plaster is mixed.

If molds are heated to above 110°C, the plaster is liable to crumble, especially at the corners, and the mold may be cracked by the internal expansion while absorbing the water from the slip. Thus a very thin slip may work great havoc among very dry molds.

[1] Lane, *Geol. Survey of Mich.*, Vol. IX.

Hope[2] mentions the use of barium chloride to make the surface of the mold insoluble, and thus prevent or reduce the wear. He says that the coating of barium sulphate formed thereby is of noncrystalline structure and does not have the necessary stability. Hence this coating of fine powder decreased rather than lengthened the life of the mold. He expressed the hope that some insoluble plaster could be found.

Ashley[3] speaks of borax, alum or tartaric acid as hardeners, but says that these retard setting and decrease the porosity which must be preserved for pottery purposes.

Simcoe[4] tells of the wear and loss of molds in both the casting and pressing processes, but says nothing of the method or composition employed in making the molds, except that 2⅛ pounds of plaster were used to a quart of water for ornamental purposes, and 2⅜ pounds per quart were used for heavier work.

Allen[5] describes the transverse bar test in determining the strength of plasters. He found that the average modulus of rupture for the first five samples was 608 pounds, which value corresponds closely with the value obtained by Grimsley. Grimsley[6] states that the strength of good plaster should be about 600 pounds. Allen speaks of the other samples as varying from 1035 to 500 pounds and says that "these results were similar to the behavior of the molds; some poor, some too good to be true." Unfortunately, he does not tell which were the best.

Eckel[7] tells of accelerators and retarders and their effect on the rate of setting, but gives no figures on the effect on strength, porosity, *et cetera*. He says, "retarders are usually of animal or vegetable origin and non-crystalline, for example glue, sawdust, blood, etc." He mentions the use of dried cactus plant and mallow root, of which two pounds were added to a ton of dry plaster. All retarders decrease the crushing strength in proportion to the amount introduced.

"Accelerators are usually crystalline salts. Common salt (NaCl) is one of the best accelerators known."

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[2] *Trans. Amer. Cer. Soc.*, Vol. XII, page 494.
[3] *Trans. Amer. Cer. Soc.*, Vol. X, page 77.
[4] *Trans. Amer. Cer. Soc.*, Vol. IX, page 187.
[5] *Trans. Amer. Cer. Soc.*, Vol. XVI, page 95.
[6] *Gypsum of Michigan.*
[7] *Cements, Limes and Plasters.*

E. Bourry[8], speaking of the wear on plaster molds, says, "this difficulty can only be partially mitigated by mixing the plaster with water with a little alum in it." Sandeman[9] says "hardness is obtained by using more plaster and less water."

Having secured a supply of good pottery plaster from the Newark Plaster Company of Newark, N. J., I set out to determine the effect of different proportions of plaster and water and the influence of retarders and accelerators on the strength and porosity of the plaster. The first idea was to make up molds with an irregular surface and test the effect of slip upon them. This was only a comparative test at best, and as all the sets of molds began to show wear after three dozen pieces of white earthenware had been cast, none could be said to be better or worse than the others. I gave up the method as requiring too much time and labor with very uncertain results.

The plaster was henceforth poured into a tin pan 9 in. by 14 in. and the rate of setting was noted by standing a thermometer in the plaster and taking a reading every minute until it was past its maximum, and had cooled for some time.

When the plaster had set, it was taken from the pan and sawed into blocks and slabs. These blocks were planed down to a bar about 3¾ inches long and $\frac{1}{16}$ in. by $\frac{1}{16}$ in. in cross section. A slab about 3 inches by 6 inches was also planed down until it was $\frac{3}{16}$ inches thick. These were marked and put away to dry for forty-eight hours at a temperature of about 85°C., after which they were put through the following tests:

The bars were used to determine the strength in a transverse test machine, and the modulus of rupture was determined by the formula $S=\frac{3}{2}\cdot\frac{pl}{bd^2}$ in which p=the load, l=the distance between supports and b= breadth and d=thickness of the bar. This modulus could now be compared to those given by Grimsley and by Allen.

The comparative hardness of the slabs was determined by arranging a jet which at a pressure of 36 inches of mercury gave

[8] *Treatise on Ceramic Industs.*
[9] *Notes on Manufacture of Earthenware.*

3500 cc. of water per minute. This jet was clamped ten inches from the face of the slab so that the jet of water hit at a right angle. The time required for this jet to wear a hole through the piece gave an indication of the hardness of the piece.

The remaining slab which made up about half of the original batch of plaster was dried to a constant weight, and after carefully weighing it was immersed in a tank of water at 20°C. in which a large block of plaster had stood for several days. This was done in order to saturate the water with $CaSO_4$, and so render the pieces immune to the solvent action of the water.

When these slabs had reached a constant weight, they were taken out of the water and drained for a few minutes, and weighed again. From these weights the percentage of absorption was ascertained. Varying amounts of salt, sodium bicarbonate, K_2SO_4, $K_2Cr_2O_7$, alum, dextrin, gum tragacanth and sulphuric acid were used.

The results are shown in Table I.

It is shown in the table that 2¾ pounds of plaster to a quart of water is the most favorable proportion, as giving high percentage of porosity and a strength close to the maximum. An addition of ½ pound plaster to a quart increased the strength quite materially, but reduced the porosity. The setting time was lengthened a little, and the temperature attained was higher. When, however, ½ pound less of plaster was used a much more porous piece was obtained, but of considerably less strength. The rate of setting was slower, and the temperature attained was lower. The strength and porosity of plaster can be governed, to a certain extent, by the proportion of plaster used in the mix as shown by Nos. 1, 2 and 3.

The rate of setting and heat of crystallization may be an index to the value of two or more plasters when similarly treated, but this rule does not apply to the value of the same plaster when treated with different accelerators or retarders. Each accelerator or retarder has its own characteristic influence.

The action of ten cc. conc. H_2SO_4 as in No. 25 gave a temperature rise of 20°C in 22 minutes and gave a porosity of 50 percent but a strength of only 230 pounds, while the action of

TABLE I

NO.	PLASTER PER QUART	ACCELERATOR OR RETARDER PER QUART COLD WATER	TEMP. RISE	TIME	MODULUS OF RUPTURE	JET TEST	ABSORPTION
	pounds		*degrees*	*minutes*		*minutes*	*percent*
1	2¾		17.5	29	685	28.0	41.1
2	2¼	Less Plaster	16.5	33	492	14.0	44.8
3	3¼	More Plaster	19.0	37	705	28.0	31.3
4	2¾	Hot Water	5 or 12	21	592	16.0	38.5
5	2¾	Stirred very little	15.0	50	581	22.0	48.6
6	2¾	1.2 grams Salt	17.5	29	568	20.0	44.8
7	2¾	12.2 grams Salt	21.0	22	533	15.0	43.3
8	2¾	2.5 grams Alum	17.5	28	508	16.0	47.6
9	2¾	10.0 grams Alum	17.0	30	560	10.0	39.8
10	2¾	50.0 grams Alum	18.0	17	392	11.0	42.2
11	2¾	1.0 grams Gum T.	15.5	45	408	13.0	41.8
12	2¾	2.0 grams Gum T.	13.5	50	424	9.0	47.0
13	2¾	5.0 grams K_2SO_4	16.5	29	616	12.0	38.1
14	2¾	10.0 grams K_2SO_4	22.0	17	625	18.0	36.6
15	2¾	25.0 grams K_2SO_4	20.0	11	594	12.0	40.7
16	2¾	5.0 grams Bicar. Soda	17.0	50	319	5.5	41.4
17	2¾	1.0 gram Bicar. Soda	18.5	54	486	7.0	37.7
18	2¾	2.0 grams $K_2Cr_2O_7$	18.0	47	544	10.0	38.0
19	2¾	5.0 grams $K_2Cr_2O_7$	15.0	35	594	16.0	37.0
20	2¾	25.0 grams $K_2Cr_2O_7$	20.0	20	420	8.0	40.3
21	2¾	10.0 grams Dextrin	16.0	45	510	16.0	36.9
22	2¾	50.0 grams Dextrin	10.0	50	638	15.0	38.4
23	2¾	1.0 Cc. Conc. H_2SO_4	17.5	47	580	13.0	42.9
24	2¾	5.0 Cc. Conc. H_2SO_4	19.5	26	319	15.0	48.6
25	2¾	10.0 Cc. Conc. H_2SO_4	20.5	22	230	11.0	50.0

12 grams of salt as shown in No. 7 gave a porosity of 43 percent and a strength of 533 pounds. The action of ten grams of K_2SO_4 as shown in No. 14 gave a porosity of only 36.6 percent with the breaking strength of 625 pounds and a temperature rise of 22°C in 17 minutes.

From these examples it is shown that these three reagents have caused a similar temperature rise and a slight variation in time, but that the results in porosity and strength vary widely. The action of retarders show similar variations, which indicates that the rate of setting is no indication to the value of treated plaster.

From the preceding table we see that the accelerators were salt, alum K_2SO_4, $K_2Cr_2O_7$ and H_2SO_4. Of these potassium sulphate was the most active, and did not cause any very serious weakness in the piece. It was noticed that as the porosity increased, the strength decreased.

Sulphuric acid had the most pronounced effect of weakening the piece, it gave the highest porosity, and was also the weakest in the transverse test. It had a tendency to soften the mold at the corners, and caused it to break off easily under the smallest strain.

Alum had a decided weakening effect in the transverse test, and failed to increase the porosity to any appreciable extent.

Potassium bichromate weakened the piece somewhat, and failed to increase the porosity; it gave the piece an objectionable color, particularly at the corners where it collected upon drying.

Salt slightly weakened the piece and increased the porosity to a slight degree.

As retarders, gum tragacanth, dextrin and bicarbonate of soda are effective in delaying the setting.

Gum weakened the piece but increased the porosity, while dextrin did not weaken the piece but decreased the porosity. Bicarbonate of soda both decreased the porosity and very seriously decreased the strength.

By the use of accelerators and retarders, we can only increase the strength by loss of porosity or vice-versa.

These tests of plaster are such as may be used readily in any factory. They should be of considerable value when correlated with the behavior of molds in actual use. An indication of the strength and porosity, the two most vital factors in determining the value of the mold, could be thus ascertained.

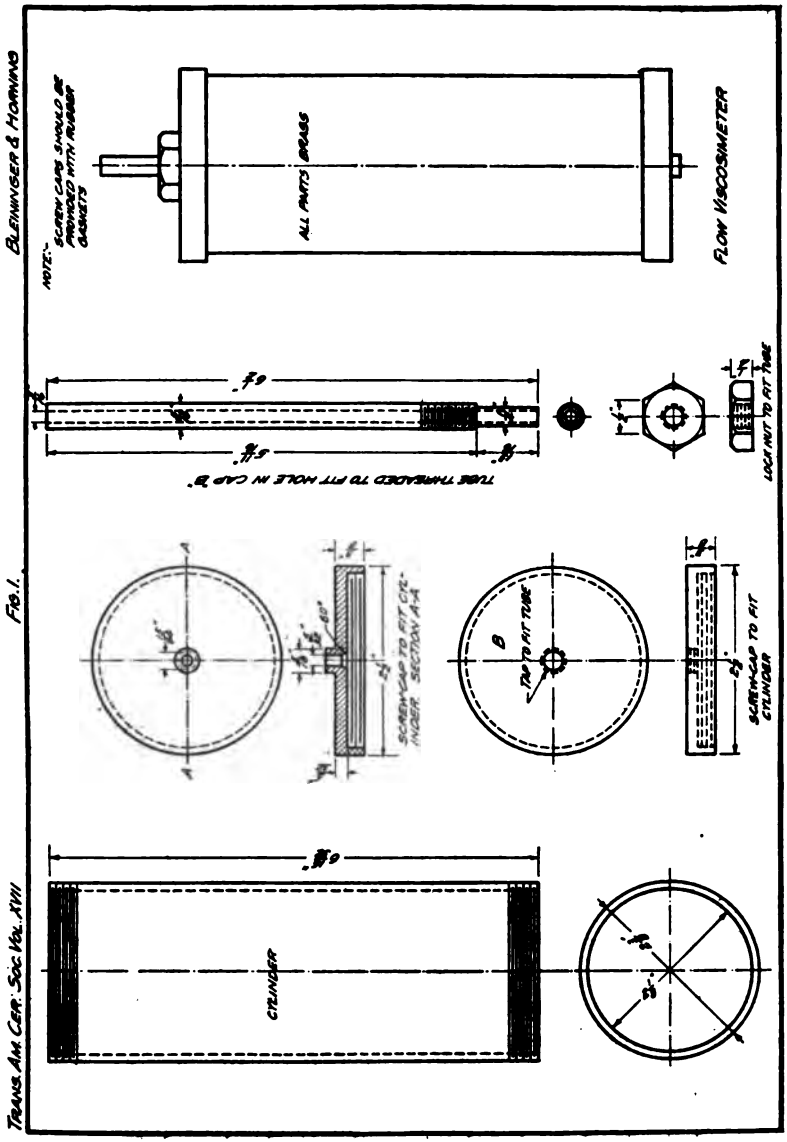
NOTES ON CASTING[1]

BY A. V. BLEININGER AND M. R. HORNUNG

The casting process coming into more and more extensive use in the clay industries offers a considerable number of problems of theoretical and practical interest. It was thought desirable to make a study of several phases of the subject.

It is quite well understood by this time that the liquefying action of the alkaline salts, sodium carbonate and sodium silicate, upon clay is due to the action of the OH ions, present in the solution. Both sodium carbonate and sodium silicate are strongly hydrolyzed in solution and yield hydroxyl ions, according to the state of equilibrium, temperature and the extent to which the Na ions are absorbed. Sodium carbonate in solution is completely ionized into $2\,Na'$ and CO_3'' ions, and these react with the OH and the H of water to form sodium hydroxide and carbonic acid respectively. Similar hydrolysis occurs with the sodium silicate. The negatively charged OH ions repel the similarly charged clay particles electrostatically. This increases the state of dispersion of the system, breaking up the larger particles into smaller ones. The water hence penetrates more deeply into the clay structure and causes the clay to "liquefy." The maximum amount of deflocculation is brought about by a definite concentration of OH ions, and if exceeded, "stiffening" will again take place, during which period the alkalinity decreases. This stage may again be followed by a second liquefaction due to absorption of the salts. Organic colloids appear to act somewhat similarly to the sodium salts in bringing about increased dispersion. But at the same time the latter seem to protect the particles against flocculating actions so that the suspension is less sensitive to the action of coagulating salts. The alkaline, fluid casting slip, in the absence of sufficient amounts of organic colloids, is at once changed to the stiffened condition by the introduction of salts like the sulphates or chlorides of lime, magnesia or aluminium. The presence of such salts in the clays, therefore,

[1] By permission of the Director, Bureau of Standards.

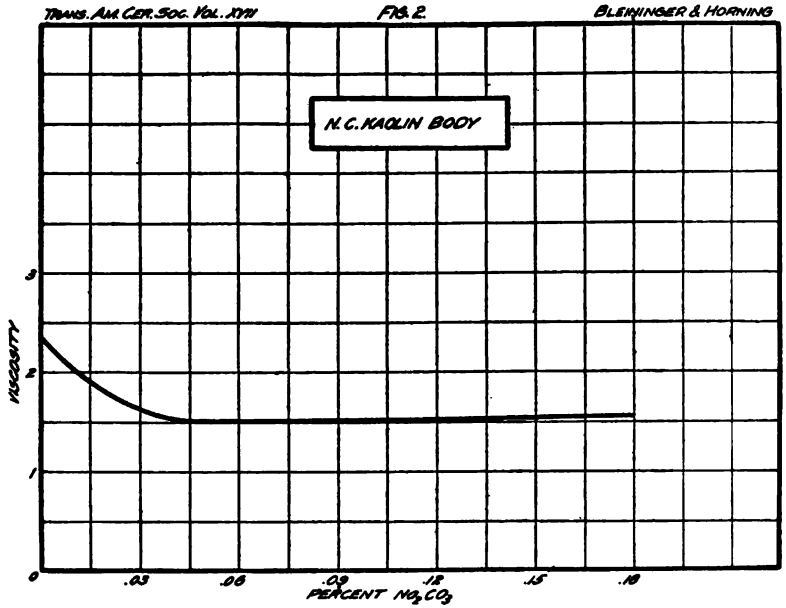

BLEININGER & HOMMING
FLOW VISCOSIMETER
ALL PARTS BRASS
NOTE:- SCREW CAPS SHOULD BE FITTED WITH RUBBER GASKETS
TUBE THREADED TO FIT HOLE IN CAP B
LOCK NUT TO FIT TUBE
SCREW CAP TO FIT CYLINDER SECTION A-A
SCREW CAP TO FIT CYLINDER
CYLINDER
TRANS. AM. CER. SOC. VOL. XVII
FIG. I.

requires not only an increased amount of alkali to bring about deflocculation, but may even render the maximum liquefaction impossible.

The principal effect of the alkaline additions to a slip, therefore, is to decrease the amount of water required to hold a unit weight of clay in the suspended state with sufficient fluidity to permit of pouring.

The practical aim in casting evidently must be to increase to the maximum the weight of clay body carried by the unit volume of the water. From 28.5 to 30 ounces per pint is the usual weight to which casting slips are carried in the case of white vitreous bodies. It is evident that the content of clay and non-plastic additions bring about variations in this respect. At the same time the composition of the body should be of such a nature that proper drainage of the water may take place from the stiffening mass to the mold. The effect of the alkaline reagents added to a slip is followed most readily and quantitatively by the determination of the viscosity. For this purpose various types of flow or torsion viscosimeters may be employed. Owing to the coarse nature of the suspensions, the accurate flow tubes of Ostwald are out of the question, and exceedingly simple devices like the brass efflux tube illustrated in Fig. 1 may be used. Here the time required for a given volume of slip, say, 200 cc., to flow through an orifice 5/32 inch in diameter is determined. The effect of the varying head due to the lowering of the level of the liquid is largely overcome by the employment of Mariotte's principle of the immersed tube. It is necessary for the proper working of the device that all joints be made air-tight. By determining the time required for the flow of water at 18°C. and dividing the observed time for the same volume of slip by this constant quantity, the viscosity of the suspension in terms of water is readily computed. For the technical determinations in question, corrections such as are necessary in the use of the Ostwald viscosimeter are not required. It was likewise found that corrections for temperature are negligible.

Of the torsion viscosimeters, the Coulomb and Couette instruments are available, while for accurate results expressed in


TRANS. AM. CER. SOC. VOL. XVII
FIG. 2.
BLEININGER & HORNING
N.C. KAOLIN BODY
VISCOSITY
3
2
1
0
.03
.06
.09
.12
.15
.18
PERCENT Na_2CO_3

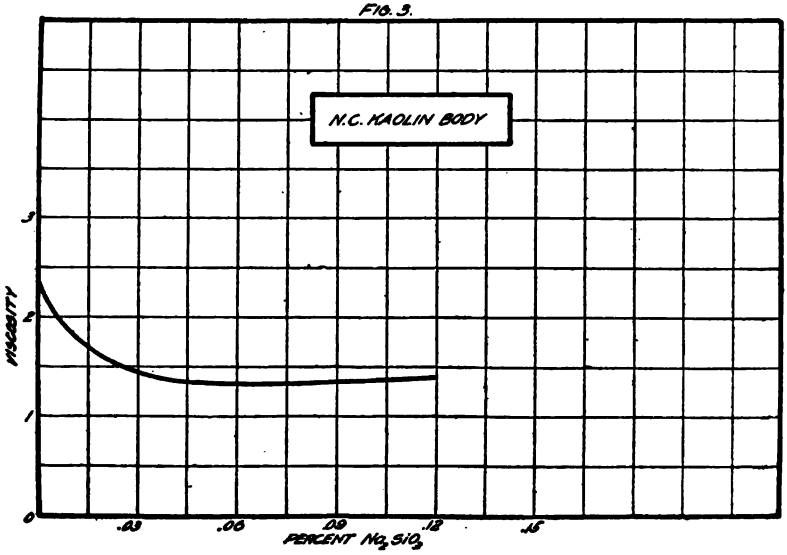


FIG. 3.
N.C. KAOLIN BODY
VISCOSITY
3
2
1
0
.03
.06
.09
.12
.15
PERCENT Na_2SiO_3

absolute units the Clark viscosimeter renders good service. The Couette apparatus represents probably the most satisfactory one for determining relative viscosity. It consists of a vessel rotating at constant speed, which contains the liquid. A metal cylinder suspended by means of a wire is immersed in the suspension. The torsion exerted upon the wire may be measured by means of a mirror attached to the projection of the cylinder, to which the wire is attached, and the angular deflection noted upon a graduated scale at a suitable distance from the instrument. Various investigators, as for instance Hatschek and others, have found the apparatus very suitable in their investigations of colloids. The flow viscosimeter as used in this work is sufficiently accurate for purposes of comparison and has the advantage of being simple and cheap.

In the study of dispersed systems of any kind, the viscosimeter may be considered as important as the use of the voltmeter and ammeter in the measurement of electrical quantities.

In general the viscosity of a disperse system may be said to correspond to the relation suggested by Einstein, Hatschek and others.

$$n_1 = n_2 \left(1 + K\frac{v_1}{v}\right)$$

where n_1=viscosity of the system;
n_2=viscosity of continuous phase (water in clay slips);
v_1=volume occupied by colloidal particles;
v =total volume;
K =constant.

In many colloidal systems, the value of the constant has been found by Hatschek to approximate 4.5 for small concentrations. Owing to the large amount of comparatively coarse material in clay and body suspensions, the Hatschek constant of the above equation cannot be expected to hold for systems of this kind, but is certain to vary with the different materials. In the case of Florida kaolin, it was found to be 5.05. Using this relation, it is assumed, of course, that the conditions of the system are practically in equilibrium, as time, temperature, adsorption and other factors are likely to bring about changes in viscosity with-

out change in the volume relations of dispersing medium and dispersed matter.

The medium which holds up the non-plastic matter in casting slips must be considered to consist of a pseudo-emulsion resulting from the further breaking down of the finer clay particles. It is essential that the viscosity of the slip be maintained sufficiently high, by the use of enough clay to prevent separation which is likely to occur in agreement with Stokes' law,

$$v = \frac{2r^2 g}{9K}(d - d_1)$$

where v = velocity of fall;
r = radius of particles;
g = gravity constant;
d = density of suspended matter;
d_1 = density of medium (water);
K = viscosity.

It will be noted from this expression, that viscosity is an exceedingly important factor in governing the rate of sedimentation. It is easy to see that the use of comparatively coarse clays, containing an insufficient amount of the emulsoid-like substance, while draining readily, might give rise to difficulties due to separation. The viscosity and other accompanying properties of a clay suspension, which is supposedly in equilibrium, do not remain constant. Variations occur with a number of factors, as temperature, time and change in the concentration of the dissolved salts due to absorption, solution or reaction. Clays, of course, differ widely in their response to the action of the alkalies. The physical structure (fineness) of clays and their chemical composition with special reference to the content of soluble salts cause them to behave differently. The previous mechanical treatment of the clay as by washing or drying is also of considerable influence.

The present work deals with the following topics.

1. The effect of increasing amount of Na_2CO_3 and Na_2SiO_3 upon the viscosity of four body slips in which the feldspar and flint are kept constant at 21 percent and 34 percent respectively.

The 45 percent of clay is introduced in succession by North Carolina kaolin, Georgia kaolin, Florida kaolin and Tennessee No. 3 ball clay. The sodium silicate used contained in the dried state 70.3 percent SiO_2 and 29.7 percent Na_2O, corresponding to the formula Na_2O, 2.44 SiO_2, which is understood when mention is made of sodium silicate throughout this paper.

2. The effect of various proportions of North Carolina kaolin body and each of the three other bodies, with reference to the viscosity of the mixtures.

3. The adsorption of Na_2CO_3 and Na_2SiO_3 by Florida and Georgia kaolin.

4. Tensile strength of bodies cast under different conditions of consistency and viscosity.

5. Calculation of the constant in general viscosity formula for different concentrations of Florida clay slips.

6. Effect of time on change of viscosity of casting slips.

EFFECT OF VARIOUS AMOUNTS OF Na_2CO_3 AND Na_2SiO_3

North Carolina Kaolin Body. This mixture was made into a slip containing 59.73 percent of solids. The viscosity was determined by means of the efflux tube already described. Two series of tests were run, one with increasing amounts of sodium carbonate and one with sodium silicate.

The Na_2CO_3 tests are shown in Fig. 2. From this curve, it is seen that there is no very large drop in viscosity and that the minimum is reached with 0.045 percent of the reagent. No tendency towards a maximum point is noted. This illustrates very nicely the deficiency in the amount of pseudo-emulsoid resulting from the use of this clay owing to its comparatively coarse nature. Either the amount of highly dispersed material is quite small or all the grains are too coarse to be affected decidedly by the reagent employed.

Sodium Silicate Series. In this case, Fig. 3, similar conditions prevail, and the minimum point is likewise reached with 0.045 percent. The drop in viscosity is from 2.35 to 1.30. It

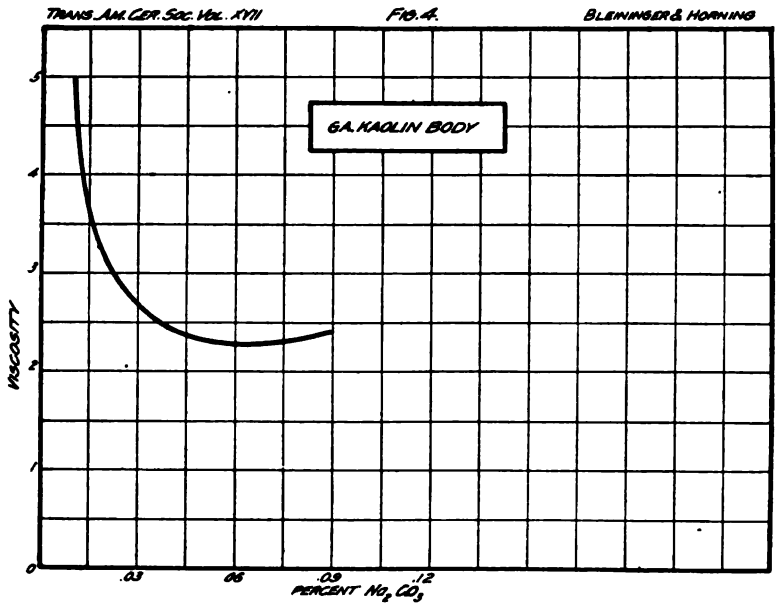
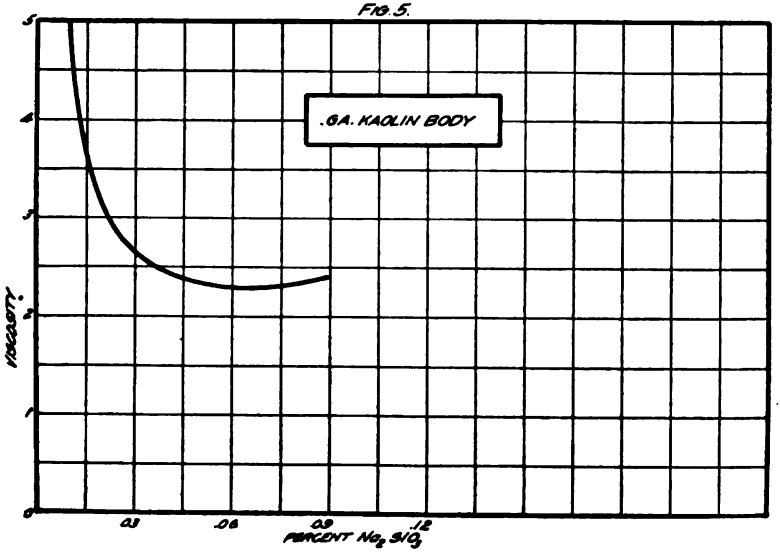

TRANS. AM. CER. SOC. VOL. XVII
FIG. 4.
BLEININGER & HORNING
6A. KAOLIN BODY
VISCOSITY
0
1
2
3
4
5
.03
.06
.09
.12
PERCENT Na_2CO_3

FIG. 5.


.6A. KAOLIN BODY
VISCOSITY
0
1
2
3
4
5
.03
.06
.09
.12
PERCENT Na_2SiO_3

appears, therefore, that owing to the comparatively coarse dispersion of this kaolin, the system is not greatly influenced by the alkali reagents.

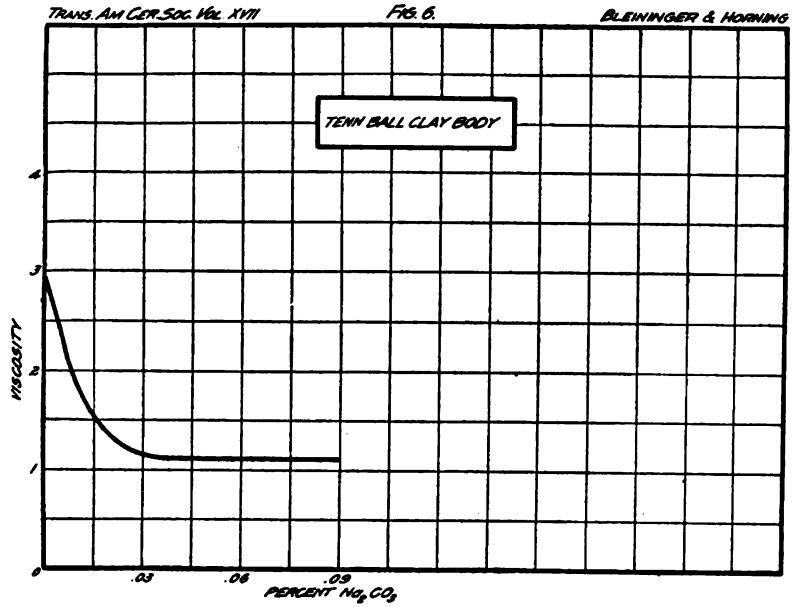
Georgia Kaolin Body. Na_2CO_3 Series. The slip used for both series contained 61.38 percent solids. From the diagram of Fig. 4, it appears that the initial viscosity is very much greater than in the case of the North Carolina kaolin body. The value was above 7 but could not be determined accurately owing to the thickness of the slip. A content of 0.03 percent Na_2CO_3 at once lowered the viscosity to 4.75, reaching a sharply defined minimum. With more than 0.045 percent of the reagents, the viscosity increases at once. This kaolin, therefore, is very sensitive to changes in the alkali concentration and hence requires greater care in regard to this point.

Na_2SiO_3 Series. In this case, Fig. 5, the minimum viscosity is reached more gradually. This point, 2.3, represents a considerably greater drop in viscosity than is the case with the carbonate. This reagent is therefore very much more effective. Although the tendency of the curve towards an increase in viscosity is clearly shown, the change is very much less abrupt than in the first case, and the range of minimum viscosity is considerably wider.

Tennessee Ball Clay Body. Na_2CO_3 Series. The slip, Fig. 6, as used, contained 47.68 percent solids. From the diagram of Fig. 6, it is seen that the drop in viscosity is 1.9 at 0.03 percent and that no well defined medium is indicated.

Na_2SiO_3 Series. Practically the same results are obtained with this reagent as with Na_2CO_3, Fig. 7. It is evident that the alkalies are being neutralized by the salts of the ball clay, but not yet sufficiently to cause flocculation.

Florida Kaolin Body. This material in the form of a slip containing 50 percent solids, was found to offer considerable difficulty in regard to obtaining constant viscosity readings. Upon making check readings the viscosity values were found to drop off continually. With increasing alkali concentrations this change seemed to become somewhat less prominent. This point


TRANS. AM CER. SOC. VOL. XVII
FIG. 6.
BLEININGER & HORNING
TENN BALL CLAY BODY
VISCOSITY
4
3
2
1
0
.03
.06
.09
PERCENT Na_2CO_3

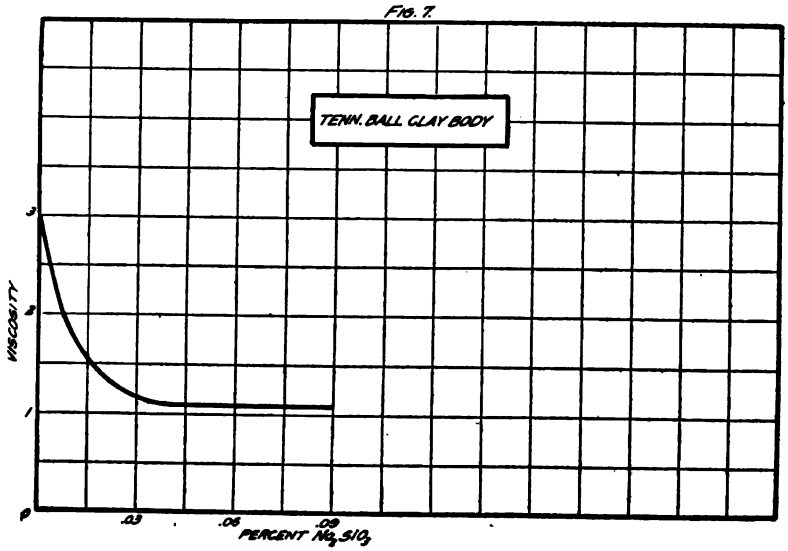


FIG. 7.
TENN. BALL CLAY BODY
VISCOSITY
3
2
1
0
.03
.06
.09
PERCENT Na_2SiO_3

may be illustrated by giving the figures for several sets of determinations, Table I.

TABLE I—VISCOSITY, WITH INCREASING AMOUNTS OF Na_2CO_3

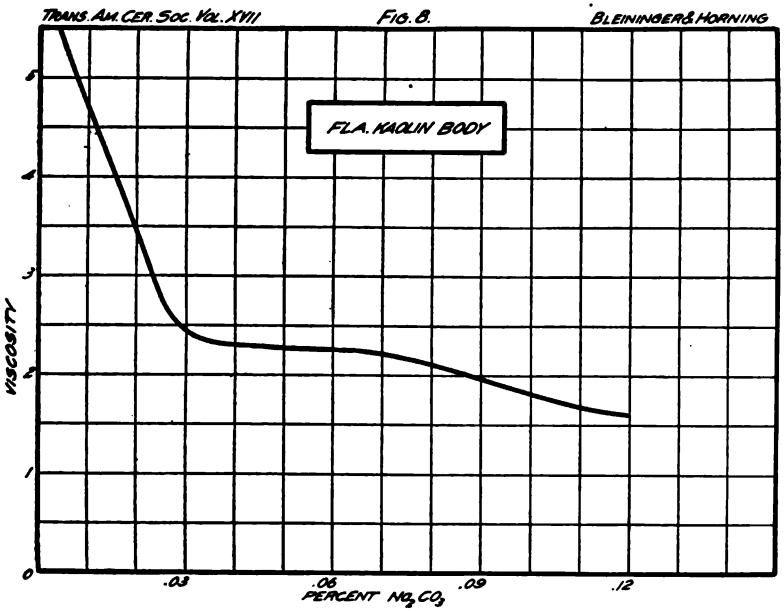
0.03 PERCENT	0.06 PERCENT	0.09 PERCENT	0.12 PERCENT	0.15 PERCENT
2.95	2.62	2.30	1.76	1.72
2.90	2.61	2.18	1.77	1.72
2.74	2.34	2.16	1.68	1.77
2.54	2.25	2.07	1.68	1.79
2.38	2.26	1.99	1.65	1.72
2.40	2.24	1.91	1.62	1.68
2.40	2.24	1.82	1.59	1.59
2.40	....	1.78	1.63	1.60
....	....	1.79	1.61	1.61
....	....	1.79	1.61	1.62

Similar variations though not so marked, were encountered with Georgia kaolin, but not with North Carolina kaolin or Tennessee ball clay. Although the slips in each case were shaken, allowed to stand for 24 hours after the alkali was added and again shaken before the viscosity determination was made, the additional disturbance caused by pouring the slip evidently caused a further liquefying effect. The preliminary drying to 110°C. did not seem to prevent these changes.

Na_2CO_3 Series, Fig. 8. It is observed from this diagram that the viscosity drop is very decided. Starting with an initial viscosity so high that it could not be determined, the addition of 0.03 percent of the reagent brought down the viscosity to 2.45. Further increments tend to lower the viscosity at a very much decreased rate, but a well defined minimum is not reached.

Na_2SiO_3 Series, Fig. 9. In this case again, the viscosity drop is very great with 0.03 and 0.06 percent of the alkali. Further additions appeared to bring about no more changes with additions as high as 0.15 percent. The sodium silicate proved to be more effective in its action than the carbonate.

In the course of this work, it was observed that upon subjecting any of the slips to a vacuum large volumes of air were


TRANS. AM. CER. SOC. VOL. XVII
FIG. 8.
BLEININGER & HORNING
FLA. KAOLIN BODY
VISCOSITY
0
1
2
3
4
5
.03
.06
.09
.12
PERCENT Na_2CO_3

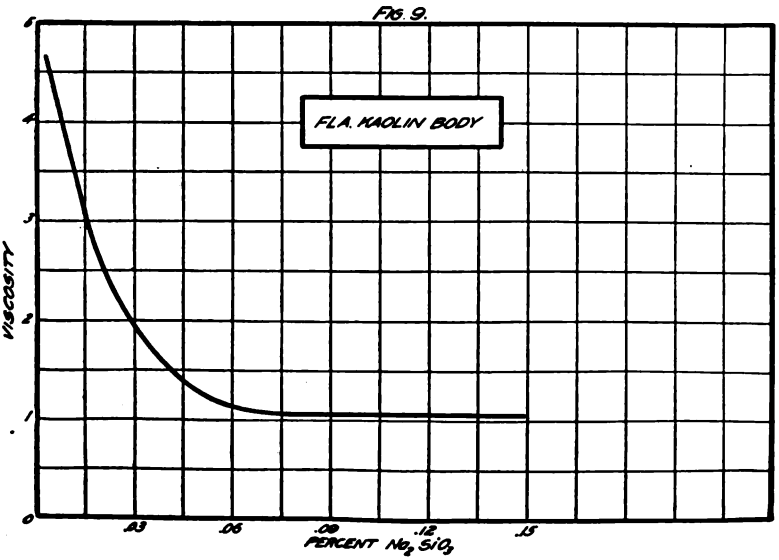


FIG. 9.
FLA. KAOLIN BODY
VISCOSITY
0
1
2
3
4
5
.03
.06
.09
.12
.15
PERCENT Na_2SiO_3

expelled even in completely deflocculated suspensions. It was thought desirable, therefore, to subject some of the slips to the vacuum treatment and to compare the viscosity of the slips with the previous value. These results are compiled in Table II.

TABLE II

KIND OF BODY	ADDITION OF Na_2SiO_3	VISCOSITY BEFORE THE VACUUM TREATMENT	VISCOSITY AFTER THE VACUUM TREATMENT
	percent		
Georgia kaolin	0.03	2.60	2.94
Georgia kaolin	0.06	2.32	2.72
Tennessee ball clay....	0.03	1.14	1.22
Tennessee ball clay....	0.06	1.08	1.08
N. C. kaolin	0.03	1.43	1.50
N. C. kaolin	0.06	1.34	1.39
N. C. kaolin	0.12	1.33	1.40
Florida kaolin	0.03	1.91	3.00
Florida kaolin	0.06	1.08	1.08

It would appear thus that a considerable amount of air is entrapped within the fine grained clays, especially in the case of the more plastic ones. This air appears to be held in a state of adsorption, as no contraction in the volume of the slip was noted. The effect was more prominent with the lower alkali concentration and with the Georgia and Florida kaolins.

In addition to these body mixtures, another body, B, was prepared containing three of these clays in the following proportions:

	percent
Feldspar	21
Flint	34
N. C. kaolin	20
Florida kaolin	20
Tennessee ball clay	5

The initial slip in this case contained 55 percent of solids. Only one series was run, using sodium carbonate. The results are presented graphically in Fig. 10. The drop to minimum viscosity, from 3.5 to 1.25, with 0.06 percent is quite marked, and

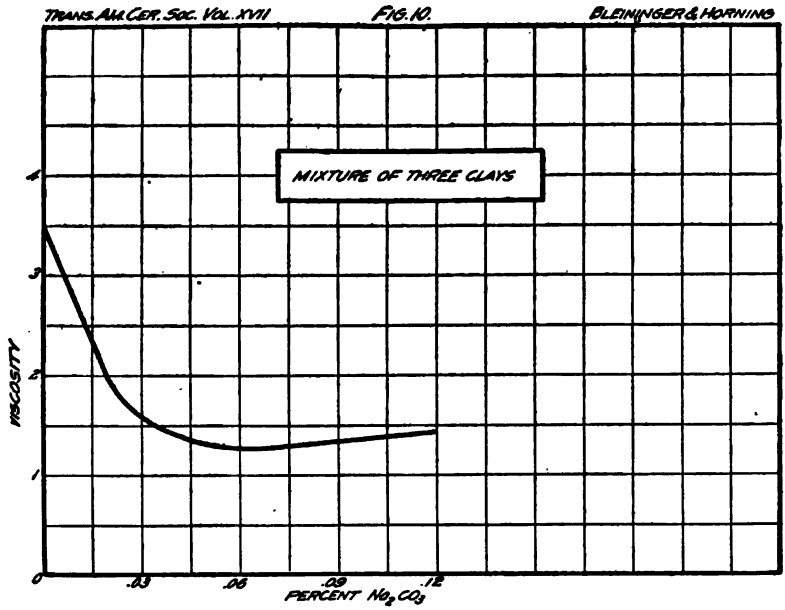
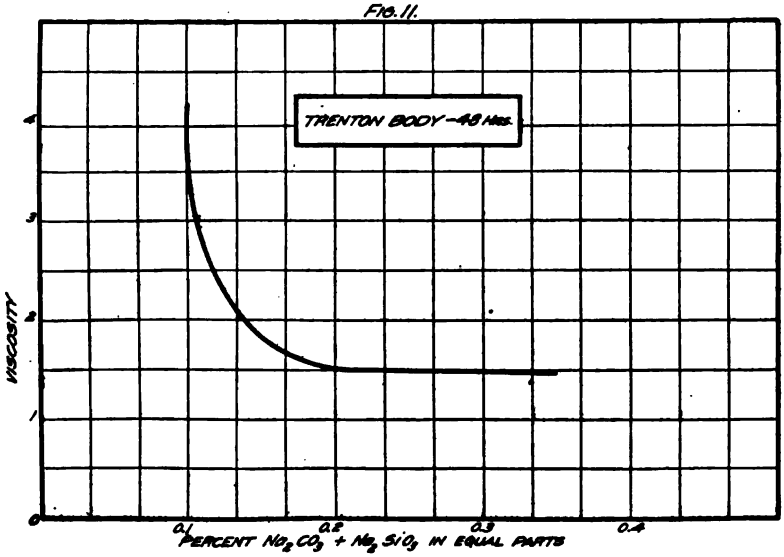

TRANS. AM. CER. SOC. VOL. XVII
FIG. 10.
BLEININGER & HORNING
MIXTURE OF THREE CLAYS
VISCOSITY
0
1
2
3
4
.03
.06
.09
.12
PERCENT Na_2CO_3

FIG. 11.


TRENTON BODY - 48 Hrs.
VISCOSITY
0
1
2
3
4
0.1
0.2
0.3
0.4
PERCENT Na_2CO_3 + Na_2SiO_3 IN EQUAL PARTS

the rise towards another maximum is clearly indicated. The coagulating tendency is very gradual, and hence the deflocculation range is of generous extent.

A commercial casting body obtained through the courtesy of a Trenton firm was likewise studied. The composition of the body was not given. In this case a mixture of Na_2CO_3 and Na_2SiO_3 in equal parts was used. The results of this test are shown graphically in Fig. 11. It appears that this body, owing to its high ball clay content, requires for maximum deflocculation a content of 0.2 percent of the reagent mixture. The viscosity of the slip, which contained 66.89 percent solids, without any addition of alkali, could not be determined. The viscosity-drop corresponding to an alkali addition from 0.1 percent to 0.2 percent is quite marked, from 4.17 to 1.5. After maximum deflocculation is attained, the condition of the slip appears to be quite constant, and there is no evidence of any coagulating tendency. About 0.15 percent of the reagents would appear to be the proper concentration for casting purposes considering no other factors, such as after-stiffening.

VISCOSITY OF CLAY MIXTURES WITHOUT ADDITION OF ALKALI

Our attention has been called to the fact that there is a certain interaction of mixtures of different clays as brought out by viscosity measurements. Mr. T. G. McDougal has informed us of interesting results obtained in this connection. In order to test out this point and to determine whether the additions of one clay slip to another caused regularly progressive or discontinuous changes in viscosity, four porcelain body slips were prepared of N. C. kaolin, Georgia kaolin, Tennessee ball clay and Florida kaolin. The body composition was the same previously employed. The contents of solids in the above order were 53.8, 53.64, 53.67 and 42.27 percent. The viscosities of these bodies were found to be 1.21, 1.08, 1.80 and 2.94. The mixtures were then made so that the North Carolina kaolin body slip was blended with each of the other three bodies in the proportion of 1:1, 2:1, 3:1, and 4:1,

on the basis of dry weights. The contents of solids for the various blends are shown in Table III.

TABLE III

MIXTURE OF BODIES	RATIO OF N. C. KAOLIN TO OTHER BODY	SOLIDS IN SLIP
		percent
N. C.-Ga. kaolin	1 : 1	53.52
N. C.-Ga. kaolin	2 : 1	53.55
N. C.-Ga. kaolin	3 : 1	53.78
N. C.-Ga. kaolin	4 : 1	53.26
N. C.-Tenn. ball clay	1 : 1	54.02
N. C.-Tenn. ball clay	2 : 1	53.60
N. C.-Tenn. ball clay	3 : 1	53.56
N. C.-Tenn. ball clay	4 : 1	53.26
N. C.-Fla. kaolin	1 : 1	51.36
N. C.-Fla. kaolin	2 : 1	53.69
N. C.-Fla. kaolin	3 : 1	53.82
N. C.-Fla. kaolin	4 : 1	53.88

The bodies before having been made up into slips were dried at 110°C.

The results of the viscosity determinations of these series are shown graphically in the diagram of Fig. 12. It will be observed that the North Carolina-Georgia kaolin series shows practically linear relation indicating no interfering phenomena in the mixture of the two systems. The case is different with the North Carolina kaolin-Tennessee ball clay series. Here, as long as the kaolin predominates, down to the ratio of 2:1 no marked change occurs. With an excess of ball clay, in the ratio 1:1, sudden coagulation occurs and the viscosity rises rapidly to a value considerably above that reached by either body slip alone. In the North Carolina-Florida kaolin series the viscosity rises with the increase in the more plastic constituent, but shows a decided drop when the ratio 1:1 is reached. The reason for this decrease is not evident. These results are sufficient to show that interaction between different clays occurs in slips, and these may have decided influence upon the behavior in the casting.

ABSORPTION OF ALKALI BY CLAY

In order to determine the degree to which clays absorb alkaline salts, mixtures of Florida kaolin, Georgia kaolin, and Georgia kaolin with 50 percent flint, were treated with solutions of NaOH and Na_2CO_3 of different concentrations. The procedure consisted in weighing out samples of the materials, adding a constant volume of the solution and rapidly filtering by suction, in a vessel containing air previously passed through KOH. By titrating for the alkali-content per cc. of the original solution and the filtrate, the amount absorbed was readily found. The results of this work are shown in Figs. 13 and 14. In the diagram of Fig. 13 the alkali content is expressed in terms of percent of the dry clay, in Fig. 14, in 0.00001 gram molecules of Na_2O. The maximum absorption of Na_2CO_3 in Florida kaolin is 0.16 percent of alkali, being 40 percent of 0.4. The amount absorbed from the more dilute solutions increases with the concentration and appears to remain constant at the above value.

The same clay mixture absorbed a far greater amount of NaOH, that is, 0.28 percent, or 56 percent of 0.5. As the absorption with both 0.4 and 0.5 percent is practically the same, it appears as if this amount absorbed was practically constant, though it is but reasonable to suppose that some reaction with the silica of the clay should occur, especially with higher concentration of NaOH.

With the Georgia kaolin-flint mixture, the absorption with 0.4 and 0.5 percent Na_2CO_3 added is practically the same, that is, 0.23 and 0.26 percent respectively. These values, therefore, appear to be practically constant for this clay.

The Georgia kaolin-flint mixture appeared to absorb about 95 percent of the NaOH added for practically all concentrations. This indicates chemical reaction with the clay, and we are evidently not dealing here with a case of simple absorption.

From these data it appears, therefore, that absorption of the alkalies plays an important role in casting slips. The greater absorption of NaOH is probably responsible for the greater effectiveness of sodium silicate in the liquifaction brought about. Whether or not the content of Na_2CO_3 is a criterion of the de-

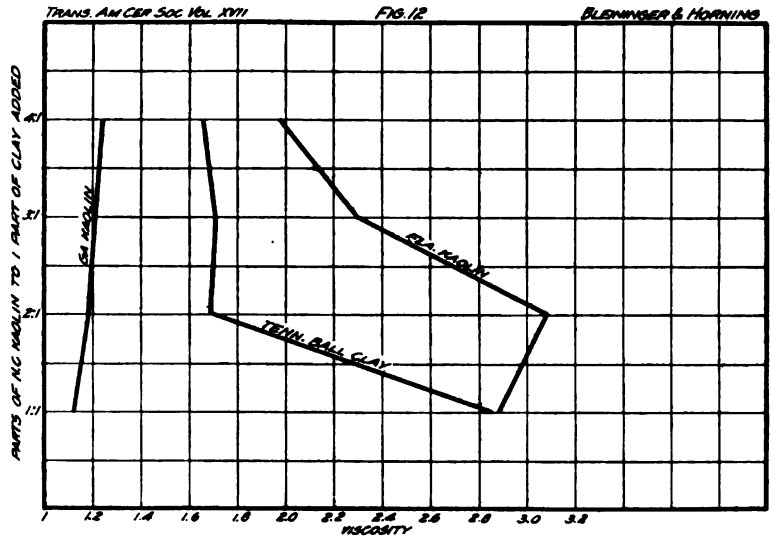
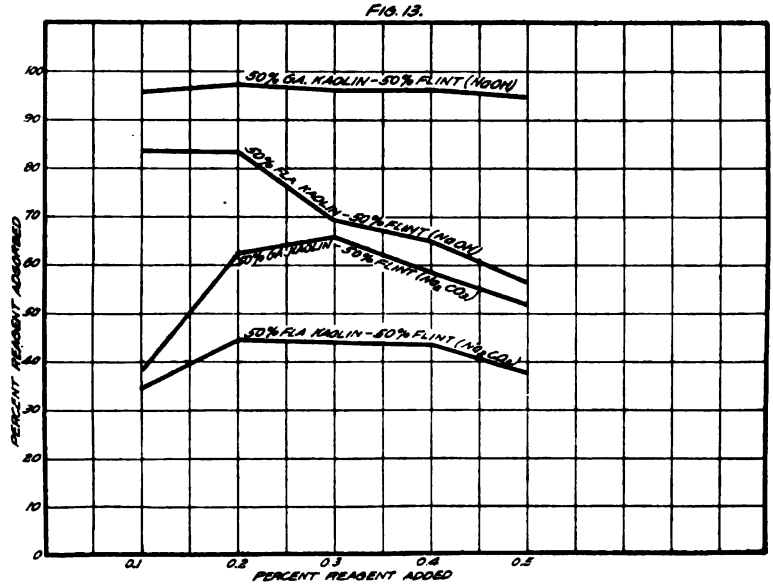

TRANS. AM CER SOC VOL. XVII
FIG. 12
BLEININGER & HORNING
PARTS OF NC KAOLIN TO 1 PART OF CLAY ADDED
4:1
3:1
2:1
1:1
GA KAOLIN
GA. KAOLIN
TEXAS BALL CLAY
1
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
VISCOSITY

FIG. 13.


50% GA. KAOLIN - 50% FLINT (H2O)
50% GA. KAOLIN - 50% FLINT (H2O)
50% GA. KAOLIN - 50% FLINT (1% CO2)
50% FLA KAOLIN - 50% FLINT (1% CO2)
PERCENT REAGENT ADSORBED
100
90
80
70
60
50
40
30
20
10
0
0.1
0.2
0.3
0.4
0.5
PERCENT REAGENT ADDED

gree of dispersion of clays remains to be demonstrated, but the indications are that it might do so.

TENSILE STRENGTH TESTS OF BODY MIXTURES

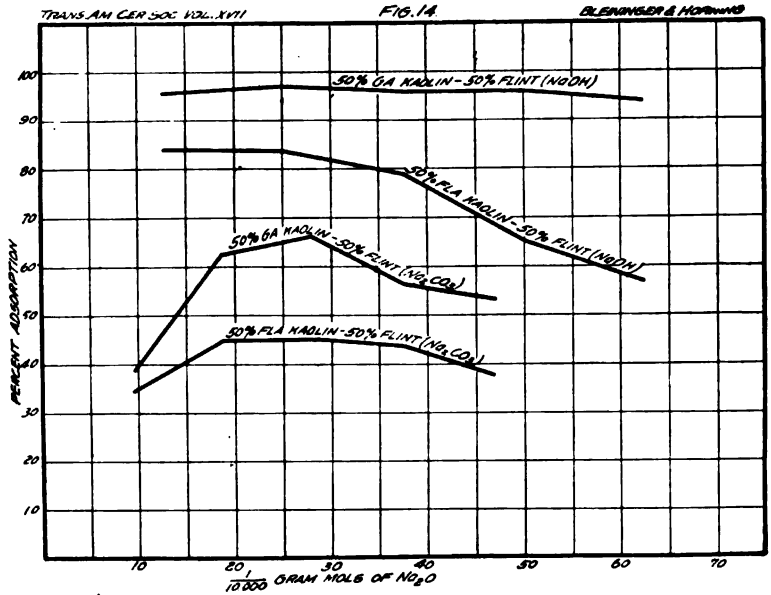
In order to throw light upon the effect of the alkaline reagents in regard to the structure of cast bodies, the tensile strength of brickettes, formed by casting in suitable plaster molds, and drying at 110°, was determined. The same single clay bodies studied before were used for this work, and three series of ten brickettes were made from each body. These were, (a) brickettes cast from the slip without addition of reagent; (b) brickettes cast from the slip with addition of Na_2CO_3 corresponding to the point of maximum deflocculation (minimum viscosity); (c) test pieces cast from slip with a concentration of Na_2CO_3 equivalent to a point to the left of minimum viscosity; (d) brickettes from slip with an addition of Na_2SiO_3 necessary to produce maximum deflocculation; and, (e) specimens from slip containing an amount of Na_2SiO_3 corresponding to a point to the left of minimum viscosity.

The same tests were also made with the casting body B. The results are compiled in Table IV.

TABLE IV

BODY CONTAINING AS CLAY	WITHOUT REAGENTS LBS. PER SQ. IN.	Na_2CO_3 MAX. DEFLOCCULATION, LBS. PER SQ. IN.	Na_2CO_3 LESS THAN MAX. DEFLOCCULATION, LBS. PER SQ. IN.	Na_2SiO_3 MAX. DEFLOCCULATION, LBS. PER SQ. IN.	Na_2SiO_3 LESS THAN MAX. DEFLOCCULATION, LBS. PER SQ. IN.
N. C. kaolin	14.9	17.8	14.0	14.7	17.2
Ga. kaolin	68.0	87.1	78.6	100.7	89.7
Tenn. ball clay	102.5	153.8	136.3	168.3	131.3
Fla. kaolin	65.7	70.5	62.4	56.5	62.5
Body B	....	67.33	73.2	59.0	91.1

From these results, it appears first, that the strength of cast bodies containing the alkaline reagents is greater than that of the bodies cast without any additions. Second, in bodies containing but a single clay, the state of maximum deflocculation


TRANS. AM CER SOC VOL. XVII
FIG. 14
BLEININGER & HORNING
50% GA KAOLIN - 50% FLINT (NaOH)
50% FLA KAOLIN - 50% FLINT (NaOH)
50% GA KAOLIN - 50% FLINT (Na_2CO_3)
50% FLA KAOLIN - 50% FLINT (Na_2CO_3)
PERCENT ADSORPTION
100
90
80
70
60
50
40
30
20
10
10
20
30
40
50
60
70
$\frac{1}{10000}$ GRAM MOLS OF Na_2O

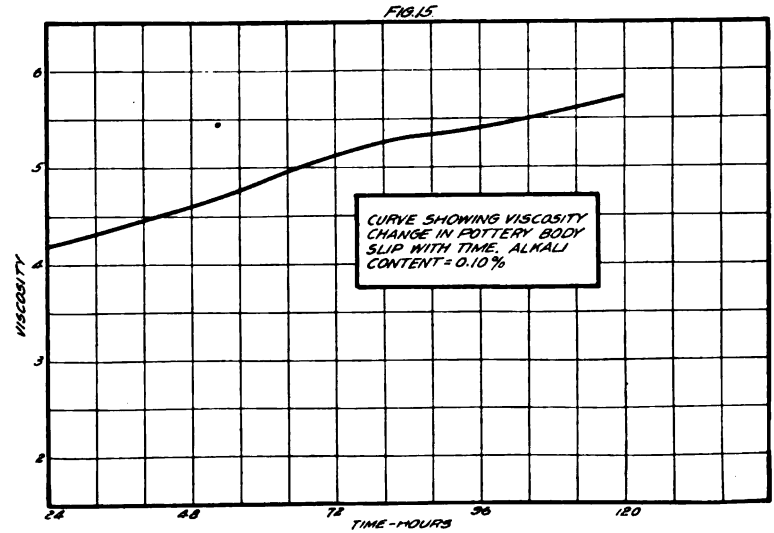


FIG. 15
CURVE SHOWING VISCOSITY CHANGE IN POTTERY BODY SLIP WITH TIME. ALKALI CONTENT = 0.10 %
VISCOSITY
6
5
4
3
2
24
48
72
96
120
TIME - HOURS

does not, as might be expected, result in weaker structure than the bodies carried to a point this side of minimum viscosity; in fact, the opposite is the case. It is possible, of course, that, owing to the small volume of the brickettes, the calcium sulphate taken up from the molds might have exercised some influence.

THE CONSTANT OF THE GENERAL VISCOSITY FORMULA

Owing to the fact that the general formula makes the assumption that the viscosity of a dispersed system composed of spherical particles is a linear function of the volume of disperse phase which we known from previous investigations is not true for clays in high concentrations, it was thought desirable to determine the constant of the expression for several concentrations of clay slips. For this purpose the exceedingly fine-grained, washed Florida kaolin was used. Three concentrations were prepared containing respectively 10.58, 18.96 and 21.23 percent of solids. The viscosities as measured by the efflux tube were 1.043, 1.55 and 2.83. Calculating the volumes of the dispersed matter by dividing by the specific gravity of the clay 2.6, and the volume of the system, we obtain for Case I:

$$1.043 = 1 + \frac{4.07}{93.49} k$$

solving for k we have the value $k=1$.

Case II

$$1.55 = 1 + \frac{7.29}{88.3} k$$

solving, $k=6.25$.

Case III

$$2.83 = 1 + \frac{8.15}{86.92} k$$

solving, $k=19.4$.

The value of k, therefore, increases rapidly with the content of solids and in using this relation for the calculation of the viscosity for any given concentration, or *vice versa*, it will be

necessary to compute this value for a series of concentrations so as to obtain a curve expressing this relation. In case such a calculation is applied to a casting slip, the percentage content of alkali in terms of the dry weight of the materials must be kept constant, or else discrepancies will appear.

Hatschek proposed for emulsoid, lyophilic, systems the relation:

$$A=\left(\frac{n}{n-1}\right)^3$$

where A=ratio of total volume to dispersed volume and n=viscosity. This relation applied to clays by the introduction of a constant,

$$A=k\left(\frac{n}{n-1}\right)^3$$

fails completely. This is not at all surprising, since clays are far from being homogeneous emulsoid systems. The formula of the type first stated, for a system composed of undeformable particles, with an appropriate series of constants, should prove useful for interpolation purposes in work of this character.

THE TIME FACTOR

The change in the viscosity of slips with time is a very important factor in casting practice. Considerable trouble ensues frequently, owing to the use of variously aged slip. Thus in one case, a slip proved to work very satisfactorily after 24 hours blunging, but showed a decided "livery" consistency, due to coagulation after three days. This phenomenon was constantly met with in the present work and was not overcome by the predrying of the clay body at 110°C. It seemed to be evident also, that the slips containing alkali just sufficient to bring about maximum deflocculation or less than this amount were more apt to show fluctuation in viscosity than those containing more than the required amount, providing the viscosity-alkali concentration did not immediately proceed towards a maximum. The time factor is explained first, by the fact that the action of the

alkalies upon the dispersed matter is often quite slow, unless vigorous agitation is kept up constantly. Second, the concentration of alkali may change also, due to absorption and reaction with silica or the soluble sulphates. The latter play an especially important part in the case of ball clays, which, as is well known, may even diminish the liquefying action of the alkalies in a very decided manner, or require the addition of an excess of the alkali. According to the nature of the clays and the content of the reagents, the time effect may consist in further deflocculation or in coagulation of the slip. Clay slips containing no alkaline reagents are subject to even greater variations in viscosity than casting slips. The accompanying diagram, Fig. 15, shows the gradual coagulation of a practical casting body containing 0.1 percent of a mixture of sodium carbonate and sodium silicate. This phenomenon does not take place with higher concentrations of alkali. It is necessary, therefore, in preparing casting slips to know the time effect, so as to counteract it by properly regulating the content of reagents. It is quite possible that the organic colloids of the ball clay may tend to exercise a protective influence on the stability of the system.

SUMMARY

The efflux viscosimeter appears to be satisfactory for the technical study of casting slips. The kinetic and temperature corrections applied in precise measurements are not necessary for the purpose in view.

Sodium silicate is a more effective reagent as far as the reduction of viscosity is concerned than sodium carbonate.

North Carolina kaolin in suspension is not influenced by the reagents in question in a marked manner, due to its comparative coarseness.

Georgia kaolin has a far greater initial viscosity than the North Carolina kaolin and appears to be very sensitive to additions of sodium carbonate. It shows a well defined minimum of short range which rapidly turns toward a maximum. Its range at minimum viscosity is greater when sodium silicate is used.

Tennessee ball clay No. 3 gives no indication of a decided minimum viscosity point.

Florida kaolin responds decidedly to the addition of sodium carbonate, but a well defined minimum is not reached, probably due to the comparatively large amount of pseudo-emulsoid or lyophile substance produced. With sodium silicate, the viscosity decrease is equally great, with no tendency to approach another maximum value.

A large volume of air seems to be absorbed in clay slips, the removal of which increases the viscosity. Thorough and vigorous stirring of the slip therefore seems essential, and exhaustion by vacuum might be beneficial. The effect of the entrapped air was more prominent with lower alkali concentrations and with the Georgia and Florida kaolins.

A body containing North Carolina kaolin, Florida kaolin and Tennessee ball clay proved to respond well to the addition of sodium carbonate but showed a turn towards greater viscosity (re-coagulation) for additions greater than 0.06 percent.

A commercial slip, fairly high in English ball clay, showed a rapid drop in viscosity, but required a much higher percent of the reagent mixture than the single clay bodies. The viscosity seemed to remain constant at the minimum value. It is possible that this condition is due to the presence of organic colloids which exercise a protective influence.

Interaction occurs between different clays with respect to viscosity changes, independent of the alkali additions, and these are not necessarily proportional to the ratios of the admixed clays, or regular in character. It is important, therefore, to know just what this interaction is, since it is quite possible that some clays may have a detrimental effect upon the others in making up the casting body. The ball clay content in a casting slip should be reduced to the minimum.

Absorption of the alkaline reagents plays an important role in casting slips. Sodium hydroxide is absorbed to a far greater extent than the carbonate and probably combines chemically with the clay.

The tensile strength of cast bodies containing alkali additions may be greater than that of the same materials cast without these reagents. Single clay body-slips, used in the state of max-

imum deflocculation do not seem to be weaker than when the suspensions are only carried to a point to the left of minimum viscosity.

The general formula,

$$n_1 = n(1+kf),$$

where f=ratio of volume of dispersed particles to total volume of system, and in which k is determined for each of a series of concentrations might prove useful for interpolation purposes, provided the alkali addition is kept constant.

Casting bodies with low concentrations of alkali are more apt to change their viscosity with time than those containing larger additions.

DISCUSSION

Mr. McDougal: I would like to call attention to a useful application in connection with the phenomena just explained by Professor Bleininger.

The viscosity variations produced by differently proportioning two or more clays, which for instance may make up the plastic content of a compounded body, is closely related to the working properties of the body in which these clays may be used.

Take, for example, some of the china clays more commonly used, viz., English Florida and Georgia. Make a water slip of each, so that all three will have the same weight per pint or unit volume. Then allow a given volume, say 200 cc. of each slip, to run from a flow viscosimeter. The English china slip will require say 45 seconds to flow 200 cc., the Florida 100 seconds, and the Georgia 35 seconds, these time readings giving relative values of the viscosity of these individual slips.

Now one would expect a mixture of English and Georgia clays to flow 200 cc., in a period of time representing an average somewhere between 45 and 35 seconds. Instead, there is a marked thickening or increase in viscosity which reaches a maximum with about 55 percent Georgia clay to 45 percent English china, which mixture requires 110 seconds for a 200 cc. flow.

Additions of Georgia clay to Florida also produce a thickening.

With additions of Florida clay to English china, however, we get a thinning or reduction in viscosity with maximum effect at about 25 percent Florida and 75 percent English, which mixture requires about 37 seconds for a 200 cc. flow.

It may be seen, then, that the addition of certain amounts of the less plastic Georgia clay to a more plastic Florida clay may produce a mixture of better working qualities than the Florida alone.

Prof. Parmelee: I would like to say to Prof. Bleininger, that in our experience with the little work we have done, we have found some clays in which the reaction went up first before it went down which rather puzzled us. I believe that Keppeler says that clays containing humic acid are quite likely to do that. I believe he demonstrated that. Has that been your experience?

Mr. Bleininger: Yes; organic material or the presence of salts may cause such a phenomenon. Clays containing free sulphuric acid would cause the curve to go up.

Prof. Parmelee: Is that a common thing to find the curve going up?

Mr. Bleininger: No, except in some ball clays. In the ordinary kaolin we would not expect to find it.

Prof. Parmelee: Did you find that in the Florida clay?

Mr. Bleininger: No, we did not.

A COMPARISON OF SOME KAOLINS IN RESPECT OF SIZE OF GRAIN

BY CHARLES F. BINNS

In view of the disastrous conditions prevailing in Europe at the present time, there have arisen certain questions as to the supply of imported porcelain, and claims have been made that wares just as good can be produced in this country from domestic clays. There are three main phases of the situation.

First. France, who stands in a class by herself as to the production of porcelain. Seger[1] stands on record in the following remarkable words: "The porcelains of Limoges excel not only in lightness and elegant shape, and in the tasteful decorative treatment peculiar to the French, but the body differs from most of the German products also in a purer, more agreeable color, in thinness and greater translucency. The superiority of the Limoges porcelains, as far as body and glaze are concerned, is undoubtedly first of all founded on the character of the raw materials available."

The French kaolin which is imported does not seem to be used in making china, and it is the opinion of several skilled potters in this country that without this clay or something equal to it, French wares cannot be duplicated.

Second, Germany. A very large proportion of the porcelain used in America comes from Germany. This is especially true of fancy wares and inexpensive bric-a-brac. Table services are not as freely imported from Germany as they are from France, though cups and saucers form a large part of the trade. Chemical porcelain is almost exclusively German. Some small quantities of German clays are imported, but these find their uses largely in the preparation of enamels for steel in which most of the early recipes called for German clay. The writer is not aware of German kaolin being used in any American china.

Third, England. Large quantities of English china and earthenware are used in this country, and at present the supply

[1] *Collected Works*, Vol. II, page 696.

has not been seriously menaced. Also, English kaolins are in constant use, and it is probably safe to say, that American china is found on English kaolin.

The facts as to the conditions abroad having been stated, this question follows: Can this country make itself independent of Europe, in the production of china-wares, by manufacturing sufficient of its own needs from domestic materials?

Dr. Charles L. Parsons in the preface to Prof. Watts' Bulletin on the Mining and Treatment of Feldspar and Kaolin (*Bulletin 53, Bureau of Mines*) says: "The Bureau's investiga-

tions have already progressed far enough to show that there can be no doubt of the United States being fully able to supply nearly all of the kaolin required for domestic consumption, and that in quality the kaolin now available in the Appalachian region is excelled by none."

Prof. Watts in the introduction to the same bulletin says: "With the establishment of pottery and kindred ceramic industries in the South, the dike products will become more easily marketable, and their use will make possible a grade of ware not approachable by the use of even the finest foreign materials."

S. W. McCallie, State Geologist of Georgia, holds three conditions responsible for the handicap that he finds against the use of Georgia kaolins in the manufacture of pottery.

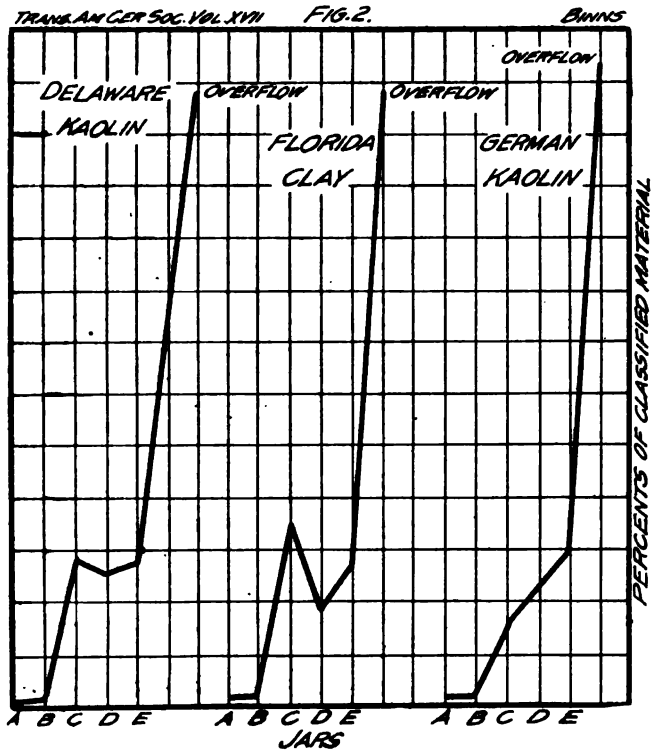
"In the first place" he says, "a large percentage of American pottery superintendents are Englishmen who learned their trade in in English potteries where English clays are universally used. These ceramic artisans, being the descendants of a long line of clay workers, are not always progressive, but are more or less prone to follow in the footsteps of their fathers. As a result of this inborn training, they are not much given to experimenting with our domestic clays, and as a consequence, they almost invariably recommend to the companies by whom they are employed the use of the English clay with which they are familiar.

Another condition which has militated against the use of Georgia kaolins in the pottery industry has been the unsatisfactory condition in which the clays have been put on the market. Here, as in many new industries, the business has suffered from the lack of trained men familiar with the modern methods of mining and washing clays. In some cases, the clays have been put upon the market in a crude condition, unwashed; and in others the length of the washing troughs has often been too short or the mesh of the screens used has been too large. In consequence, the clays have not been prepard with the same degree of care as the English clays with which they must compete, and they are, therefore, not so uniform in physical and chemical properties, conditions which are of prime importance to the pottery industry. Heretofore, our clay mines have sacrificed quality for quantity. Their object seems to have been large tonnage with low values instead of small tonnage and high values. The net results of this method of putting kaolin on the market has been low prices and an uncertain market.

These conditions acting against the use of the Georgia kaolins in the pottery industry are now, in a large degree, remedied by all of our large producers. Not only have they erected modern clay refining plants at much expense, and put them in operation, but they also employ as managers, trained men familiar with every phase of clay mining and refining. The plants which have adopted these up-to-date methods are constantly extending their market and increasing their output with a corresponding increase in the profits from their sales.

A third condition which works against the Georgia clay industry is the unequalization of freight rates between domestic and foreign clays. That is to say, the freight rates by rail in this country are very much higher on domestic clays than on foreign clays. A concrete example of the injustice in freight rates is as follows: The

freight rate on a ton of English clay in carload lots from New Orleans to Chicago is $2.00, whereas, the freight rate on a ton of clay from the Dry Branch clay district of Georgia to Chicago, although a shorter haul by more than 300 miles, is $4.20. There would be some justification in this discrepancy in freight rates, provided the Georgia clays brought a higher market price than the English clay, but the opposite condition prevails. It is true there is a protective duty of



$1.25 per ton on all china clays imported into this country. Nevertheless, as long as foreign clay producers are permitted to deliver their clays to inland consumers at such a great freight rate reduction, the domestic clay producer is not only not protected by the Federal government, but at the same time it, through the Interstate Commerce Commission, permits the common carriers to exact a premium from the domestic product in the form of increased freight rates which far overbalances the protective tariff."

These are the statements of scientific men and investigators. Turning now to the manufacturers, there are not many opinions on record, though several could be quoted from hearsay. At the annual convention of the United States Potters' Association held in December last, the vice-president, Mr. Charles Gosser, who was elected president at the same meeting, said: (The report is taken from *"Pottery and Glass"*).

"I urge you, gentlemen, to assume an independent attitude. 'Made in America' is a slogan. Herald it from the housetops. Don't say 'just as good as import.' Scorn the comparison and turn the batteries of your foreign competitors against themselves by declaring your uncompromising belief that the best evidence of pre-eminence is that it is made in America. I would further commend to your most diligent attention the standardizing of a fundamental body of both earthenware and china composed exclusively of American clays and materials. My attention has been recently called to the Federal government's laboratory efforts in this direction. With a scientific staff of government chemists we may expect incalculable help and hasten the day of the American potter's supremacy.

We greet this as the advent of government patronage such as has for centuries been bestowed upon the potters of Europe. On the western continent and within our reach, fairly bursting to surface for freedom are untold treasures of kaolin, spar and all ingredients employed in the making of chinaware."

No opinion is here expressed as to the foregoing quotations nor are they being considered as in the same category as that which follows. In a popular journal boasting a very large weekly circulation there was published in the issue of January 23rd an article entitled *The Silent Shuffle*. In this the author says:

"In the United States, Germany and other European countries have sold an enormous quantity of white china. Now there are two things that American manufacturers might do: They could sit down, like Micawber, and wait for something to turn up; or they could get out and turn something up. They are doing the latter.

A pottery man from Trenton, New Jersey, has been very active. He went into Ohio shortly after the war commenced and looked around. Today he is preparing to operate the first plant in America that will make a certain kind of chinaware. He means to supply a product as good as any that every came from Germany. For this a great market opens for him. It is a market not free from technical difficulties and selling problems; but who can doubt that the coming

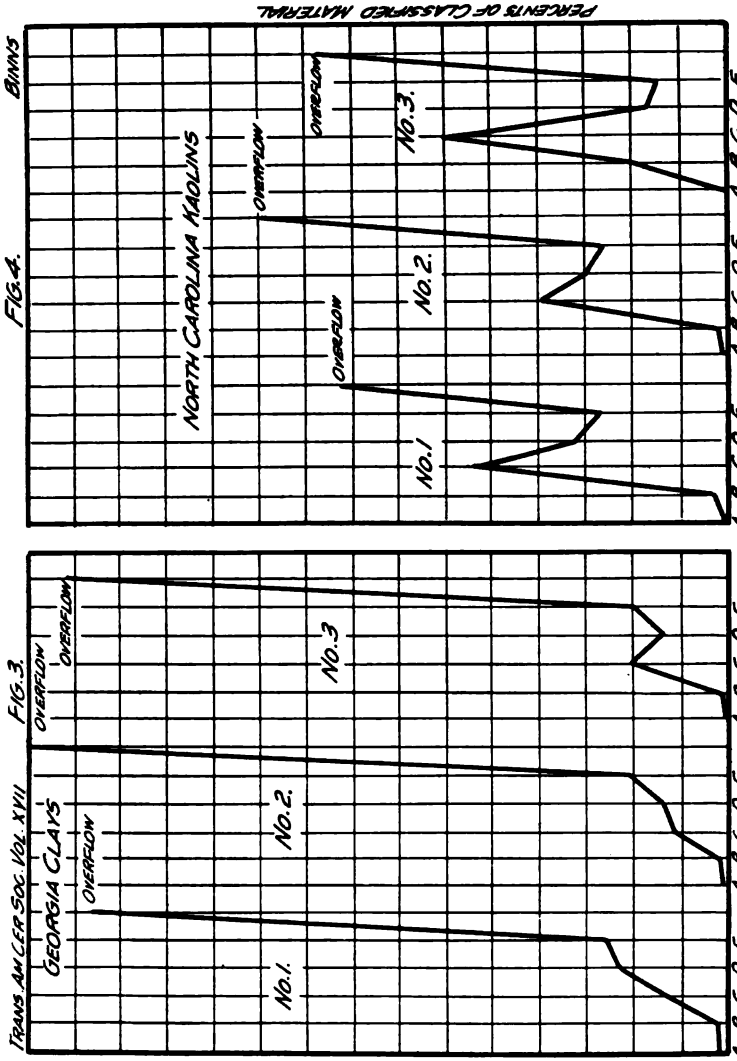


FIG. 4.
BINNS
NORTH CAROLINA KAOLINS
OVERFLOW
OVERFLOW
OVERFLOW
No. 1
No. 2.
No. 3.
PERCENTS OF CLASSIFIED MATERIAL
A B C D E
A B C D E
JARS
FIG. 3.
TRANS. AM. CER. SOC. VOL. XVII
GEORGIA CLAYS
OVERFLOW
OVERFLOW
OVERFLOW
No. 1.
No. 2.
No. 3
A B C D E
A B C D E
JARS

decade will see American pottery manufacture enormously increased and thousands of additional workers employed?

A certain pottery in Ohio has been idle for two years previous to the war. It manufactured, in its day, yellow crockery. Since the war the company has been reorganized and today is employing a hundred and fifty hands—not on yellow dishes but on high-grade semiporcelain.

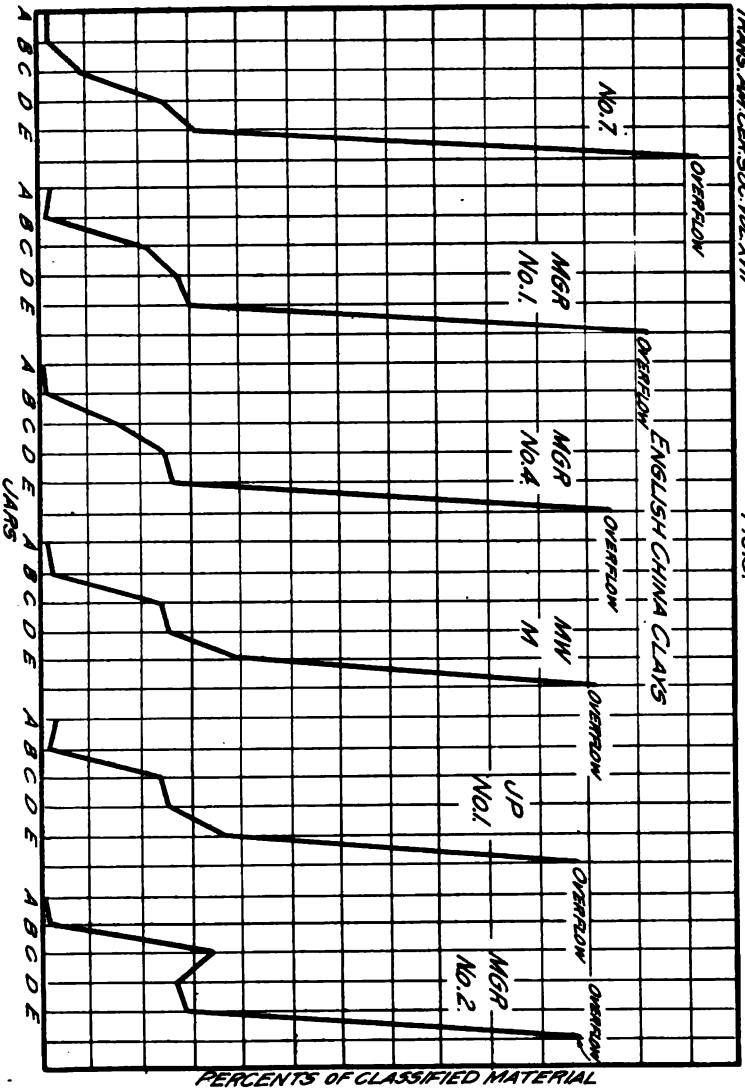
Right along this line the United States Bureau of Standards, at its Pittsburgh laboratories, is now making tests with American clays. It is certain already that American raw material can be produced that will not be surpassed by that used in any foreign pottery or china. At East Liverpool, Ohio, a company has just been formed to develop large deposits of native clay. At the same time comes the report of government investigation that plenty of kaolin—used in pottery manufacture—exists in the southern Appalchian region, and of the best quality."

All of these quotations point towards an affirmative answer to the question put. The authorities quoted evidently believe that this country contains clays which are equal if not superior to imported clays, and that wares can be made from them which shall be superior both to European wares and to domestic wares made from imported clays.

This discussion has been seething in the mind of the writer for many years. He is as anxious as any one can be to answer the question in the affirmative and with bold assurance. Numbers of clays have been examined from time to time, and the present study aims at presenting only a single series of facts.

The practical qualities of a kaolin depend upon certain properties. Among these, two may be considered of prime importance, color, and size of grain. The latter point only is under consideration. The investigation has been carried out rather irregularly during the last two years in the course of teaching work, and upon such clays as came conveniently to hand. The apparatus used is that originally devised by Schultze, adapted in the laboratory at Alfred and since used by Ashley, Watts, and others.

To the original three receptacles of 5.0, 7.5, and 13.5 cm. diameter, there have been added two others of 21.5 cm. and 30 cm. diameter respectively. This gives a velocity of water-flow (upward carrying current) from 1.5 mm per second through .7,


TRANS. AM. CER. SOC. VOL. XVIII
FIG. 5.
ENGLISH CHINA CLAYS
No. 7.
OVERFLOW
MGR No. 1.
OVERFLOW
MGR No. 4.
OVERFLOW
MW 11
OVERFLOW
JP No. 1.
OVERFLOW
MGR No. 2.
OVERFLOW
BINNS
A B C D E
A B C D E
A B C D E
A B C D E
A B C D E
A B C D E
JARS
PERCENTS OF CLASSIFIED MATERIAL

.18, .08 and .04 mm, the finest materials being that carried away by a .04 mm. per sec. flow.

The method consists of a thorough deflocculation and an elutriation continued to clear water. A period of 48 hours has sometimes been necessary to secure perfect separation.

Several English china clays, one German kaolin of unknown locality and American clays from North Carolina, Delaware, Georgia and Florida have been used in the study.

The curves plotted are really a series of six points, and they indicate a vertical measure only. The points are joined to produce a graph, but the horizontal spaces have no significance. Figure 1 is simply to show the increase of the area of the vessels and the consequent diminution in upward carrying current.

In most china clays the amount left behind by a flow of .7 mm per second is almost negligible, rarely amounting to one percent. The third vessel seems to be a critical point. It is the amount indicated at this step, which expresses the grain of the clay. The percentage of material here varies widely. Some of the clays show less than five percent and others more than twenty-five percent. From this point on, the variation is smaller, though, of course, the amount of the finest material varies indirectly as that of the coarsest.

An inspection of the curves will show that the English, the German, and the Georgia clays are generally very similar in grain. Some of the English clays which are usually considered of less than first quality show the break in the curve caused by the large content of coarse grains; but this is most marked in the clays from North Carolina, all of which carry an excess of grains of this size.

No attempt is here made to interpret these results nor has any comparison of color been made. It is expected that these features will form the basis of a second study.

DISCUSSION

Mr. Mayer: I would like to ask if you made any surface factors?

Prof. Binns: I did not. I did not get the actual size of grain carried off by the flow.

Mr. Mayer: Some time ago, when I started to make vitrified china, I started with the North Carolina clays. In stopping the manufacture of semi-porcelain, I had some clays left that were of extremely good color, and those of you who know anything about clays, know that as a rule North Carolina clays runs a better color than European clays. There are clays mined today in North Carolina that are superior to any clays I have ever seen. Now some of you are familiar with this statement I am going to make, but it just bears out the statement made here. When I first started in the manufacture of vitrified china, I had some very good North Carolina clay, and after conducting a number of experiments and deciding on what kind of a body I would use, I determined that I could get a very good colored piece of ware, all conditions being favorable, from this North Carolina clay. So I made up an experimental body, and when it came out of the kiln, the ware showed no sign of vitrification at all, absolutely nothing, and I supposed that some big error had been made and threw the whole business away and started in again and was very, very careful in the second weighing out, to see what had been done that was wrong. The second batch came out exactly the same as the first, and while I did not throw the second lot away, I threw it to one side and made the third batch, because I simply could not understand what I was up against. Well, when the third lot was made, the results were just the same. I want to say, that I have been using right along, North Carolina clay in a semi-porcelain body, which practically all the potters do west of the Alleghenies; I don't know what they do east. I was unable to understand what this meant. For a long time I had been using the elutriation test for determining the size of grains, in fact, I use it altogether, keep my records of all materials received, in that way. After some little correspondence with some of our friends who knew the elutriation test a little better than I did or knew the apparatus, and after reading the articles that appeared in the *Transactions*, I decided that 12,000 was the surface factor for feldspar; that anything less than 12,000 I would look upon with a good deal of suspicion; if any better than that, I thought it was all right, and as a rule, it runs very uniformly about those figures.

I took some of the English clays I was using and found the surface factor of some of these English clays to be in the neighborhood—I am speaking from memory entirely—of 16,000, that is, between 16,000 and 17,000. If I remember rightly, I tried two clays that were on the market; one was M. W. M., the other M. G. R. No. 2. If I would take the size of grain of the North Carolina clay, I could not get more than 8,000 and 9,000. Well now, the consequence was that with the temperature I had, it would not fuse. The North Carolina clays are beautiful clays as regards color but are not fine enough as regards grain to use for that purpose. I saw some chemical porcelains made by Prof. Bleininger that were of just as good color as any German or French porcelain I ever saw, and I know that was all made from North Carolina material. It was shown on this diagram that the fineness of the Georgia clays agrees closely with that of English clays, but is there anybody that ever had any experience with Georgia clays who ever found a Georgia clay good enough in color to use, unless you go deep enough? Georgia clays which do show a very fine grain are not, however, clays that we can use with any great amount of certainty, because of the uncertainty in the mining of the clay. The trouble about the clay, that is, all I have ever seen, is that it has a great deal of titanic acid in it; the oxide of iron in it is very low. There are some potteries in the west that are making ware absolutely of American material; I used to do that myself some years ago, but it is simply impossible to do it today.

Mr. Hice: I would like to ask Prof. Binns if I am right in assuming that the North Carolina clays are residual and the Georgia clays, so called, sedimentary kaolins?

Prof. Binns: Dr. Ries has told me that North Carolina clays are true kaolins and Georgia and Florida clays are sedimentary. They seem to occupy an intermediate position, partly ball clay and partly kaolin.

Mr. Hice: They have been transported and relaid quite a number of times?

Prof. Binns: I don't know about that.

Mr. Bleininger: I was very much interested in the paper by Prof. Binns and I want to congratulate him on carrying on this work, for the reason, that he has used velocities which separate materials approaching the limit between microns and submicrons. It has been shown that velocities below two tenths of a milimeter per second will separate the most important part of clays, the clay substance proper. I was interested in seeing his figures. It seems to me that he has struck the keynote of one of the most important parts of clay study, namely, the differentiation of the fine grains. We have studied this question to some extent, though not so extensively as Prof. Binns assumes, but we have made attempts along this line to find out whether or not it is possible to improve our methods of washing, and Mr. Brown has a paper on this subject.

Mr. Watts: I would like to ask if others who have worked along this same line, particularly Bureau of Standards men, have not found that the preliminary treatment to which the clay is subjected before it is elutriated, has a very positive effect upon the results of the classification? Have you found anything of that sort, Prof. Bleininger whether or not if the clay is allowed to stand for quite a long while in water, or whether if it is simply worked up, agitated, sufficiently to bring it into slip form and then elutriated, it gives you a different classification when you elutriate it this way?

Mr. Bleininger: I want to say, that we have found that the previous history of all the clays is very important, but not so much so in this connection as in casting. Every slip, even without any addition of alkali, continues to change constantly. We have checked this by means of viscosity measurements. We have found continuous viscosity changes. Our experience shows that the presence of salts or alkalies in clays will greatly affect elutriation results.

Mr. Watts: I want to say, to a certain extent, in self-protection, that the statement which prefaced the work of *Bulletin 53* was never satisfactory to me. I think it is an inference which Dr. Parsons drew from the general figures given and which

should properly have been qualified. It was not my intention, and I think I brought it out in the body of the Bulletin, to intimate that the North Carolina kaolin was a source of supply to which the American potter could turn to as a substitute for English kaolin or English china clay. I think that point was brought out, but the point was made that with these materials alone it was possible to produce a class of ware which from an art standpoint, particularly, would be equal or superior to practically anything that we obtained from Europe. That would necessarily mean that the process of manufacture, the method of burning, and a good many other things, would have to be changed more or less. The ultimate product in itself, I am convinced, could be made of wonderfully high quality. The main point with regard to those kaolins which I was endeavoring to bring out and which impressed me in the investigation, was that there is in the South Appalachian an enormous amount of material located in small deposits, which, if a proper method of handling could be developed, would furnish a very great supply, but which, under the present system of one company working a deposit and then moving on to another deposit and working it without trained help, was not producing the class of results which we ought to expect.

Prof. Binns: I am very glad to hear Prof. Watts say that. When I made that statement I rather hoped he would say just about what he has said. When I quoted him, I specifically said that he had alluded to dike products, not exclusively to kaolin. At the same time I give him credit for saying exactly what he believes to be the case, and I do not want to be understood as criticising any of those opinions in any way. I found, as would be expected, the greatest possible difference in the clays, in their yielding to deflocculation methods. I worked a sample of North Carolina clay without deflocculation, simply agitating it in distilled water and then deflocculated another sample of the same clay, and found a marked difference. The North Carolina clays are difficult to deflocculate. Taking a standard solution of NoOH, it took 60 cubic centimeters to treat 20 grams of North Carolina kaolin, whereas 5 cubic centimeters would treat a Georgia kaolin

completely, but I treated each one with what I found to be its maximum electrolyte. There is another point I want to raise in that connection and that is something upon which you can enlighten me. I think Ashley stated that his deflocculation was done on a basis of a given weight of salt to a given weight of clay, but I found that it is the degree of concentration of the electrolyte, rather than the amount of salt present to the weight of clay that does the work. It takes exactly the same concentration to deflocculate 30 grams of clay as 50.

Mr. Bleininger: You are right; it is the concentration of the alkali in the liquid which is most important.

Mr. Watts: I would like to say further in regard to these North Carolina kaolins, kaolinization has apparently proceeded only to the point where the transition from feldspar to kaolinite has actually occurred. I am convinced that the subsequent process which must have occurred in European kaolins, and which have caused them to be so fine grained, is lacking. You do not find in Europe, so far as I know, either in England or on the Continent, enormous quantities of semi-kaolinized material in portions of these dikes. The dike is well advanced as regards plasticity and as regards kaolinization. In North Carolina and throughout the South Appalachians you find large areas where kaolinization has only progressed a very short distance. I brought out in *Bulletin No. 53* the fact that you find the amount of water of crystallization to progress all the way from one half of 1 percent right up to your theoretical 14 percent. The progress of kaolinization is evidently indicated by the content of combined water. Even after kaolinization has apparently been completed, you will find, by covering the entire area, that you will obtain all degrees of plasticity. I found at one or two points deposits of North Carolina kaolin which indicated by elutriation a fineness of grain and a degree of plasticity under bonding strength equal to the English kaolin, but not in many instances. The process of separation of the kaolin, like all true American processes, has just been carried far enough to permit the product to be marketed—absolutely no further. Of course that is a commercial proposition. I know that a very much more plastic pro-

duct might be obtained if that process were carried a little further, but the American potter can and does use the material, and pays within 50 cents as much per ton for a material which is floated through 400 feet of trough as he would pay for that floated through about 800 feet of trough, and which would reduce the total output about 20 percent. The proposition is perfectly plain, it would not pay to eliminate that 18 percent or 20 percent more material for the sum of 50 cents more per ton. The proposition simply resolves itself into what the potter is willing to accept and what he will take. Furthermore, these North Carolina kaolins are quite variable as regards impurity, and to eliminate these impure streaks would add very greatly to the most of production and that increased expense is not justified in the judgment of the men who are mining at present, because of the fact that the trade takes practically all they manufacture under present conditions.

Mr. Purdy: I wish Mr. Mayer would state his experience with American ball clays as compared with English ball clays. Our desire is to find a clay that not only gives good color but has a strong bonding property in the green state as well as sufficient plasticity to give it tight body. Have we an American ball clay that will match the English ball clay in this respect?

Mr. Mayer: We have always used in manufacturing semi-porcelain a little over half American ball clay, the remainder being English ball clay of two different kinds. When we began the manufacture of china, we used a plastic ball clay from Tennessee mined by the Johnson-Porter Clay Company, their No. 9, and up till the last few months we were using this clay right along. It has better color than the English ball clay; its vitrification is just as good, and the clay was very much less expensive. Now that clay has given out, and I am anxiously awaiting some trials that were being made of some clays when I came away—Kentucky clays—that will possibly take the place of those clays that were so successfully used. There are clays in Kentucky that are of god color and good strength, and I think a great deal of the Tennessee clay being used now in place of English clay. There is a prejudice against the Tennessee clay; I don't know

why. I have not used a pound of English ball clay until recently and I think that in a very short time I will be out of the use of it again. There are clays that we have used very successfully; I speak of these Tennessee clays particularly. There are some of them the color of which, as a rule, is better than that of the English ball clay. Some of them do not vitrify as well and possibly are not quite as plastic, but this particular clay I spoke of was certainly as plastic as the English ball clay and had the great benefit of a lower price. I am using a Tennessee ball clay but it is not as good as I used to have, and as I think; in a short time I will have, and when I get it I will be very glad to let you know about it.

FELDSPAR POSSIBILITIES IN GEORGIA[1]

BY S. L. GALPIN

Highly feldspathic rocks (pegmatites) have been found throughout that portion of Georgia which is underlain by formations of the Crystalline Belt.[2] The area includes parts of the Appalachian Mountains and the Piedmont Plateau and occupies the territory north of a line (the Fall line) drawn from Columbus, through Macon, to Augusta, but excepting several counties lying in the northwest corner of the state, where only Paleozoic rocks are found. This excepted portion may be roughly marked off by a boundary extending from Murphy, N. C., southwest through Cartersville to the Georgia-Alabama line.

The pegmatitic rocks occur in the form of lenses, dikes and irregular masses which intersect gneissis, schists, granites and other crystalline rocks. The lenses vary in width from a few inches to nearly one hundred feet. The length in outcrop is usually from four to eight times the thickness. Oftentimes several lenses are connected, forming irregular sheets. It is usual to find a grouping of the lenses into bands or zones which show a N. E.-S. W. trend following the schistosity or foliation of the metamorphic rocks into which they have been intruded. Such belts have been traced in some cases as much as 40 or 50 miles, and may extend farther. The lens-like bodies may lie in any position, but usually dip to the southeast at angles of from 30° to 70° with the horizontal.

The dike-like bodies are bounded by more nearly plane surfaces and as a rule dip more steeply than the lenses. While the majority strike with the country rock, yet some of the most important representatives cut sharply across the intruded rocks' foliation and strike nearly N.-S., or less often, E.-W. Most of the dikes are narrow, relatively few exceeding a width of 10 feet. Some, however, reach a width of 100 feet or more.

[1] By permission of the State Geologist of Georgia.
[2] Feldspar and Mica Deposits of Georgia. *Ga. Geol. Survey, Bulletin 30, 1915.*

The irregular masses range in diameter from a few feet to possibly fifty yards. They are less common than the preceding types, although of wide spread occurrence.

Practically all outcrops of pegmatite are decomposed to some extent. Weathering usually begins along fractures and in the finer textured portions of the deposits. In this way both fresh and decomposed material may be found in the natural outcrops. Usually the disintegration and decay decrease with depth, however, instances have been noted where decomposed material is abundant below an apparently sound outcrop. The depth to which kaolinization of the feldspar may extend is limited by the position of the permanent ground water, which varies from a few to perhaps 100 feet below the surface in the Piedmont. Possibly a greater range may exist in the mountains. In general those pegmatites found in the mountains are more sound than those of the Piedmont. There are, however, wide differences in the condition of individual deposits in each province. Marketable kaolin has resulted from this decay in some cases but generally, the material found near the surface is too badly stained by limonite to have any value. These variations in condition are probably due to textural inequalities primarily, but peculiarities of topography, erosion and ground water circulation have been contributory factors.

Texturally one may divide the pegmatitic rocks of Georgia into three groups as follows: (1) Those bodies which are largely of coarse texture; (2) Those having mainly a primary, medium or fine texture; (3) Those of medium or fine textures which have resulted from dynamic metamorphism.

The representatives of group 1 are usually dike-like bodies less than eight feet wide, although a few of larger size have been found. The constituent mineral grains or crystals may vary in diameter from a few inches to as much as three or four feet. In a few instances, a banded arrangement of the minerals suggests fissure vein development as do also the occasional vugs noted particularly in mica bearing pegmatites. Deposits of this group give the most promise as possible sources of high grade feldspar because of their texture, composition, and condition, since the

principal constituents are microcline (potash feldspar) and quartz. Plagioclase (soda-lime feldspar) and muscovite are usually present in minor amounts, while biotite, tourmaline, beryl and garnet have been noted in some cases. Weathering is usually less complete in these coarse textured rocks than in the following types.

Pegmatites having the medium texture of the second group are usually of dike-like form, but do also occur in lenses. Probably the largest feldspathic deposits of the State are of this type. Their resemblance to coarse granite is marked, the main difference lying in the greater irregularity of the pegmatite. Single masses of feldspar one foot or less in diameter are usually irregularly scattered through these dikes. Chemical analysis and microscopic examination of this coarser material shows it to be potash feldspar. Surrounding these larger anhedral masses is a granite-like mixture of quartz, with both potash and soda-lime feldspars biotite, muscovite and small garnets. Not infrequently there appear to be dikes of the first group included partly or wholly within some of the second.

The third group of pegmatites is usually represented by lens-like bodies. Whatever the original texture of the rock may have been, crushing and recrystallization have since resulted in an irregular intergrowth of rather small grains of quartz and the feldspars. Mica, especially sericite is always present, while garnet and biotite are usually rather abundant. Because of the intimate admixture of deleterious minerals, the feldspar of this type of deposit gives little promise of value. However, owing to their more rapid weathering, they may in some cases provide marketable kaolin.

While there are many pegmatitic deposits within the State, yet few of them possess sufficient size to warrant consideration as possible feldspar producers. In the following brief descriptions of some of the more promising occurrences, an attempt is made to give only such details as are generally characteristic and economically important.

Pegmatite dikes of the coarse textured type and ten feet or more in width have been found in several counties. Smaller bod-

ies of the same type are more numerous and wide spread. The following descriptions are representative of the range in this type of deposit.

In Monroe County a single outcrop of a dike 12 feet wide occurs 1½ miles west of Juliette. The dike has a N.-35° W. strike and nearly vertical dip. It is composed largely of feldspar in crystals and aggregates from 4 to 15 inches in diameter. From 10 to 20 percent of quartz, a little muscovite, and traces of biotite are also present. A chemical analysis of an average specimen may be found in Table I. Microcline is the principal feldspar as shown by microscopic examination. The deposit is not badly weathered and is favorably situated for quarrying. The distance to the Southern R. R. is 1½ miles.

In Putnam County, near Lynchburg, a dike is exposed along the Central of Georgia R. R. 100 yards east of Little River. The dike is of the compound type and varies in width from 10 to 20 feet. The coarse feldspar of the dike is in irregular masses free from injurious minerals other than a little quartz. Its quality is indicated by analysis No. 2 of the table. The balance of the dike is made up of a fine graphic granite. The exposure is considerably weathered and not of sufficient extent to allow of an estimate of the amount of coarse material present without considerable further prospecting.

From three to five miles north, and northeast of Elberton, Elbert County, there are several coarse grained pegmatites. The best exposure lies one-quarter mile north of the Beaver Dam bridge on the Ruckersville road and three and one-half miles northeast of Elberton. The dike, which is nearly vertical, has a total width of eighteen feet, ten feet of which is composed of nearly pure feldspar of good quality as shown by analysis No. 3. Weathering has not affected many of the dikes to a harmful extent. This belt of pegmatites appears to continue to the northeast for a distance of several miles. No promising deposits were found at a distance of less than 3½ miles from the nearest railroad.

Several old mica pits and prospects in eastern Rabun County lie along the general N.-S. strike of what seems to be an unusually

long pegmatite dike. From the Kell mine on the north to the McCracken prospects on the south is a distance of possibly eight miles. Feldspar of excellent quality has been removed from the Kell mine (see Analysis No. 4) in the process of mica mining. The dike here is about 24 feet wide, and largely of coarse texture. Quartz and muscovite are common associates with the feldspar. Garnet is occasionally found, and beryl has been reported. Biotite is scarce. The dike narrows toward the south, and in other prospect pits especially at the Beck,[3] and Tunnel workings there is considerable kaolin. While conditions for quarrying are usually good, yet there is little promise of feldspar production from these deposits, as they are all more than eight miles from the nearest railroad.

In Habersham County, badly decomposed pegmatites of considerable size and rather coarse texture occur along the Tallulah Falls R. R., between the Falls and Turnerville. No fresh material appears in these exposures, and there is reason to believe that weathering extends downward a considerable distance.

Several other deposits of coarsely crystallized feldspar have been found, especially in some of the mica bearing pegmatites of Hall, Lumpkin and Union counties. They are apparently less extensive than those already described, but may prove of value in connection with the mica.

The medium- or fine-textured pegmatite dikes of large size are somewhat more common than the variety which has been considered. They also appear to be more persistent along the strike although the width may be highly variable from place to place.

In eastern Troup County, dikes of a medium- and even-textured pegmatite are numerous, and are well exposed along the Atlanta, Birmingham and Atlantic R. R. near Knott station. Some of these deposits attain a width of 50 feet, but none was seen in which single masses of feldspar exceeding one foot in diameter could be found. The exposures are all considerably kaolinized, especially the parts of finer texture. Besides feldspar, the type rock contains a low percent of quartz together with

[3] Watts, A. S., Mining and Treatment of Kaolin. *U. S. Bureau of Mines, Bulletin 53, 1913*, p. 118.

muscovite and some biotite. An analysis of the more sound feldspar is given. (No. 5.) This analysis is doubtless above the average for the deposit, and as the rather uniform texture of the rock would not be favorable to much sorting, one could not expect to obtain a spar of high quality here.

Pegmatite of similar nature is abundant for the distance of several miles to the north-east of this locality, and the belt probably continues beyond the central part of Meriwether, the county adjoining Troup, on the east.

A few outcrops of medium-textured pegmatite in dikes reaching a maximum width of 25 feet were found along public roads from two to five miles south-west of Grays, Jones County. These dikes are characterized by a pink feldspar which on analysis proved to be rather high in soda (see analysis No. 6). Microscopic examinations of some of the material demonstrated the presence of microcline, albite and orthoclase. Small (microscopic) scales of mica are abundant in many of the feldspar grains, apparently as inclusions, rather than as a weathering product.

There are several rather widely separated pegmatite dikes of considerable size in Madison County. One lies four miles north-west of Comer and one-eighth mile above Thompson's Bridge over Hodge Creek. The main dike is of irregular width with a maximum of perhaps 70 feet. The texture is irregular, there being scattered masses of feldspar and quartz as much as 15 inches average diameter. There is a strong suggestion of dynamo-metamorphic structure in parts of the dike. Quartz is rather abundant as is also muscovite in small scales and shreds. Biotite and garnet are to be found. Analysis No. 7 is thought to be representative of the average material obtainable here.

A 40 foot pegmatite is exposed in Copper Mine Creek, one-fourth mile south-west of the Southern Railway's Station at Hiram, Paulding County. The bulk of the dike is composed of a coarse, granite-like mixture of feldspar, quartz, muscovite, and traces of biotite and garnet. Evenly distributed through this matrix are elongate, anhedral masses of feldspar from five to ten inches in length. These two rather distinct portions of the dike

TABLE I—ANALYSES OF GEORGIA FELDSPARS[1]

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10
Moisture at 100°C	.....	.....	.04	.....	.03	.....	.07	.04	.04	.04
Loss on ignition	.....	0.18	.62	.....	.14	.18	.50	.36	.30	.50
Soda (Na_2O)	1.97	1.09	3.34	2.56	3.09	4.13	3.15	2.80	4.26	7.84
Potash (K_2O)	9.87	14.84	11.48	12.46	11.81	7.10	4.02	8.44	1.86	1.44
Lime (CaO)	.42	.....	.03	none	.24	none	.88	.23	2.07	.56
Magnesia (MgO)	none	.03	trace	trace	.06	.22	.03	.04	none	.08
Alumina (Al_2O_3)	15.14	21.08	20.38	19.86	17.80	13.89	15.96	17.06	16.92	16.68
Ferric oxide (Fe_2O_3)	1.62	0.40	.24	.18	1.44	1.28	.80	.48	.80	.48
Ferrous oxide (FeO)	.....	.....	.03	.....	.....	1.01	.....	.....	.....	.03
Manganous oxide (MnO)	.....	.....	trace	.....	.....	.10	.....	.....	.....	.00
Titanium dioxide (TiO_2)	.....	trace	trace	.....	.04	.09	trace	none	.02	.01
Sulphur trioxide (SO_3)	.....	.....	.....	*	.....	.05	.....	.....	.....	.....
Phosporus pentoxide (Pe_2O_5)	.....	.....	.....	0.19	.....	.18	.....	.....	.....	.....
Silica (SiO_2)	71.04	62.74	63.75	64.75	65.00	71.86	74.41	70.70	74.17	72.36
Total	100.06	100.36	99.91	100.00	99.65	100.09	99.82	100.15	100.44	99.66

[1] Tabulated from *Bull. 3, Ga. Geol. Survey.* Dr. E. Everhart, Analyst.

* Undetermined.

No. 1. Pegmatite; near Juliette, Monroe Co., Ga.
No. 2. Coarse feldspar; near Lynchburg, Putnam Co., Ga.
No. 3. Coarse feldspar; 3½ miles N. E. from Elberton, Elbert Co., Ga.
No. 4. Coarse feldspar; Kell Mica Mine, Raburn Co., Ga.
No. 5. Selected feldspar; near Knott Sta., Troup Co., Ga.
No. 6. 5 miles S. W. Grays, Jones Co., Ga.
No. 7. Pegmatite; 4 miles S. W. of Comer, Madison Co., Ga.
No. 8. Coarse pegmatite; near Hiram, Paulding Co., Ga.
No. 9. Fine pegmatite; near Hiram, Paulding Co., Ga.
No. 10. Pegmatite; Robertstown, White Co., Ga.

were analyzed separately (No. 8 and No. 9 of the table) with interesting results. The coarser material is clearly a potash feldspar, while, in the matrix, it is equally definite that the predominating feldspar is one of the members of the plagioclase group.

In the vicinity of Robertstown and Nacoochee Valley, White County, there are numerous outcrops of granitic pegmatite, many of which have a width of from 50 to 100 feet. These dikes show resemblance to the Paulding County deposit. Analysis No. 10 gives the approximate average composition of one of the smaller dikes of the region. Microscopic examination of material from another dike indicates that the coarser feldspar is mainly orthoclase with subordinate microcline, while the more granite-like portion of the rock is largely plagioclase with quartz, muscovite and a little biotite. The potash feldspar, although present in the largest grains was apparently the last to crystallize.

Similar, but usually more deeply weathered deposits are found in several other countries. Only the most sound and favorably located dikes of this type are considered as even possible producers of feldspar on a permanent commercial basis.

The transportation costs from Georgia to either Trenton or East Liverpool eliminate any but the best grades of feldspar from competition in those markets. For this reason it may be that the exploitation of the Georgia feldspar deposits must wait until higher prices are paid, or a more local market established.

Department of Geology and Mining,
Iowa State College,
Ames, Iowa

WHITE TERRA-COTTA GLAZES AT CONES 6 AND 7

BY ERCILL C. HILL, NEW YORK CITY

The terra-cotta glazes in this study are of the Bristol type, but are made more complex by the addition of barium and tin oxide to the usual bases, lime, zinc and potash. They differ in this respect from the stoneware and porcelain glazes investigated by Purdy in Vols. IV, V, XIII and XIV, *Trans. Amer. Cer. Soc.* They also differ from the terra-cotta glazes investigated by Parmelee, Vol. IX, and Parmelee and Heidingsford, Vol. XIV, in that they contain tin oxide. The object of the work was to study the effect of the different components in the glaze, particularly zinc and tin oxide. The purpose of the experiments was not to cover a large field of compositions, but to work within limits, in which, in the judgment of the writer, practical results are possible, and by making small variations in composition to cover the limited field somewhat thoroughly.

Materials used were: feldspar, whiting, zinc oxide, tin oxide, barium carbonate ball clay and flint. The formula of the feldspar calculated from the analysis is — $KNaO$, $1.34\ Al_2O_3$, $8.01\ SiO_2$, combining weight 704. A rational analysis of the ball clay gave:

Clay substance	70.25
Feldspar	20.65
Quartz	9.10

The glazes were calculated from the molecular formula by multiplying the equivalents by their equivalent weight, using 258 for the equivalent weight of clay, as if pure clay were used. Since the ball clay contains only 70.25 percent clay substance, we divide the weight of pure clay by .7025 to get the ball clay required. The amount of feldspar and quartz contained in the ball clay is then calculated, and this is deducted from the weight of feldspar and flint in the formula. The percentage composition of the glazes is then calculated.

Preparation of Trials. Five hundred grams of each glaze was weighed separately, and ground thirty minutes in small

porcelain jar mills. The glazes were sprayed on smooth tiles pressed from a terra-cotta body containing about 30 percent of grog, and over which a white underslip had previously been sprayed. The underslip and glaze were kept as uniform in thickness as possible.

The trials were fired in a 15 foot, up-draft muffle, terra-cotta kiln, using oil as the fuel. The average length of burn was eighty hours. Two sets of trials were fired at cone 7 and two at cone 6.

VARIATION OF R O

The glazes were divided into five groups in which the feldspar varied from .35 to .15 equivalents. Each group was divided into three series, in which the SnO_2 content was varied from .10 to .20 equivalents. Each series contains 20 members in which ZnO is increased from 0 to .30 equivalents. The CaO and BaO make up the remainder of the R O. The Al_2O_3 and SiO_2 remain constant at .50 Al_2O_3, 4.00 SiO_2 for Group I to III where the feldspar ranges from .35 to .25 equivalents. Since the clay would be too high for groups IV and V—.20 and .15 equivalents feldspar—if the same Al_2O_3 and SiO_2 content were maintained, this was lowered to .325 Al_2O_3, 2.75 SiO_2 for these groups. The molecular formula of the glazes are given in Tables I, II, III, IV, V.

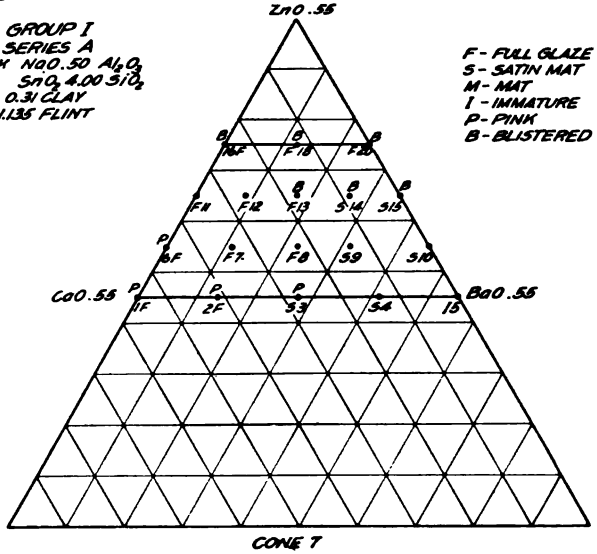
The results at cone 7 are shown graphically on the triaxial diagrams. Since the three series of each group differ only in their SnO_2 content and as there is not a great difference in the appearance of the trials of the different series, only one series of each group is plotted. On the diagram the gloss of the different members are shown by the letters **F**, **S**, **M** and **I**. **F** indicates full glaze, a bright, glossy glaze; **M**, mat; **S**, satin mat, a glaze having a gloss between a full and mat glaze, and **I**, immature. Glazes having a pink cast are marked **P**, and those that are blistered, **B**.

None of the trials were crazed when drawn from kiln. There was no crawling or cracking of the glaze on these flat tile.

FIG. 1.

GROUP I
SERIES A
.35 K NaO .50 Al_2O_3
.10 SnO_2 4.00 SiO_2
0.31 CLAY
1.135 FLINT

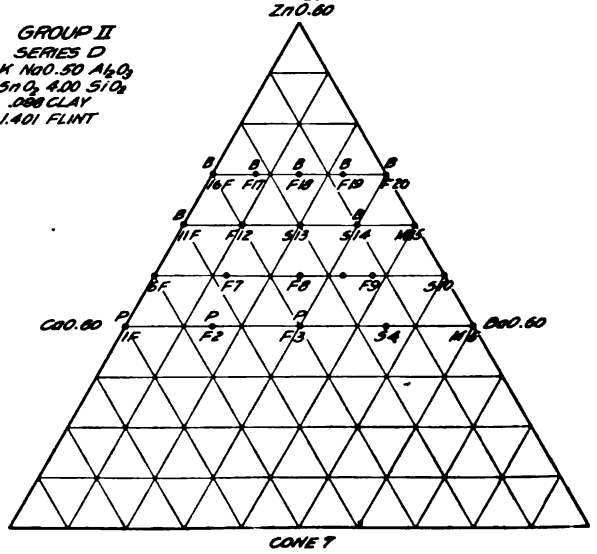
F - FULL GLAZE
S - SATIN MAT
M - MAT
I - IMMATURE
P - PINK
B - BLISTERED



CONE 7

FIG. 2.

GROUP II
SERIES D
.30 K NaO .50 Al_2O_3
.10 SnO_2 4.00 SiO_2
.088 CLAY
1.401 FLINT



CONE 7

Group I. See Table I. Gloss.—There is not a great difference in the gloss of the three series of this group, in which the SnO_2 is increased from .10 eq. in Series A to .20 eq. in Series C. When SnO_2 replaces CaO, there is a decrease in gloss, but when it replaces BaO, the gloss remains about equal.

When ZnO replaces CaO, the gloss increases up to .10 eq., but remains about equal with further additions. But when ZnO replaces BaO, the gloss increases with increase of ZnO throughout. When there is no ZnO in the glaze, No. 1, high lime, has the best gloss. Since the amounts of CaO and BaO decrease with increase of ZnO, the difference in gloss between the members having

$$\frac{CaO}{BaO}=\frac{1}{0} \text{ and } \frac{CaO}{BaO}=\frac{1}{1}$$

becomes less and less, until with .30 eq. ZnO, the gloss is about equal. With the higher ZnO contents, the members having

$$\frac{CaO}{BaO}=\frac{3}{1}$$

have a trifle more gloss than the others. When the ratio of CaO to BaO is less than 1:1, the gloss decreases rapidly with increase of BaO. The gloss at cone 6 is much less than at cone 7.

Opacity. The opacity and white color of the glazes increase with increase of SnO_2. It also increases with increase of ZnO, and with increase of BaO when the ratio of $\frac{CaO}{BaO}$ is less than 1:1. Increase of SnO_2 is more effective in increasing opacity than either ZnO or BaO.

Pink color. A decided pink color is developed in some of these glazes. The intensity of color and the members that are pink, decrease from Series A to Series C. None of the members of Series C are pink. Since the SnO_2 increases from Series A to Series C at the expense of CaO and BaO, it is not evident whether the decrease of pink color is due to increased SnO_2 or diminished CaO and BaO. The pink color decrease with increase of ZnO. None of the members with .20 or more ZnO are pink.

Number 3, $\frac{CaO}{BaO}=\frac{1}{1}$, and no ZnO, has the deepest pink color. The intensity of color decreases from No. 3 to No. 1, $\frac{CaO}{BaO}=\frac{1}{0}$.

TABLE I—MOLECULAR FORMULA, GROUP I

CONSTANT .35 KNaO, .50 Al_2O_3, 4.00 SiO_2

		SERIES A CONSTANT SnO_2=.10		SERIES B CONSTANT SnO_2=.15		SERIES C CONSTANT SnO_2=.20	
No.	ZnO	CaO	BaO	CaO	BaO	CaO	BaO
1	0	.55	0	.50	0	.45	0
2	0	.412	.137	.375	.125	.337	.112
3	0	.275	.275	.25	.25	.225	.225
4	0	.137	.412	.125	.375	.112	.337
5	0	0	.55	0	.50	0	.45
6	10	.45	0	.40	0	.35	0
7	10	.337	.112	.30	.10	.262	.087
8	10	.225	.225	.20	.20	.175	.175
9	10	.112	.337	.10	.30	.087	.262
10	10	0	.45	0	.40	0	.35
11	20	.35	0	.30	0	.25	0
12	20	.262	.087	.225	.075	....	....
13	20	.175	.175	.15	.15	.125	.125
14	20	.087	.262	.075	.225	....	....
15	20	0	35	0	.30	0	.25
16	30	.25	0	.20	0	.15	0
17	30	....	....	....	....	....	....
18	30	.125	.125	.10	.10	.075	.075
19	30	....	....	....	....	....	....
20	30	0	.25	0	.20	0	.15

With .10 eq. ZnO No. 6, $\frac{CaO}{BaO}=\frac{1}{0}$, is the only member pink. At cone 6 the pink color is less intense, and fewer of the members are pink.

Blistering. Blistering increases with increase of ZnO. All of the members with .30 eq. ZnO are blistered at cone 7 and some with .20 eq. ZnO. There was no blistering in any of the

series with ZnO below .20 eq. Of the glazes with equal ZnO content, those with the higher SnO_2, have decidedly the most blistering, and those with the higher BaO have slightly more blistering than the others. None of the glazes in any group were blistered in the two burns at cone 6.

TABLE II—MOLECULAR FORMULA, GROUP II

CONSTANT .30 KNaO, .50 Al_2O_3, 4.00 SiO_2

		SERIES D CONSTANT SnO_2=.10		SERIES E CONSTANT SnO_2=.15		SERIES F CONSTANT SnO_2=.20	
No.	ZnO	CaO	BaO	CaO	BaO	CaO	BaO
1	0	.60	0	.55	0	.50	0
2	0	.45	.15	.412	.137	.375	.125
3	0	.30	.30	.275	.275	.25	.25
4	0	.15	.45	.137	.412	.125	.375
5	0	0	.60	0	.55	0	.50
6	10	.50	0	.45	0	.40	0
7	10	.375	.125	.337	.112	.30	.10
8	10	.25	.25	.225	.225	.20	.20
9	10	.125	.375	.112	.337	.10	.30
10	10	0	.50	0	.45	0	.40
11	20	.40	0	.35	0	.30	0
12	20	.30	.10	.262	.087	.225	.075
13	20	.20	.20	.175	.175	.15	.15
14	20	.10	.30	.087	.262	.075	.225
15	20	0	.40	0	.35	0	.30
16	30	.30	0	.25	0	.20	0
17	30	.225	.075	....	....	....	....
18	30	.15	.15	.125	.125	.10	.10
19	30	.075	.225	....	....	....	....
20	30	0	.30	0	.25	0	.20

Group II. See Table II. Gloss. The group is less glossy than Group I. The gloss increases in all series with increase of ZnO. There is not a great difference in the gloss between the members having $\frac{CaO}{BaO}=\frac{1}{0}$ and $\frac{CaO}{BaO}=\frac{1}{1}$, but those with $\frac{CaO}{BaO}=\frac{3}{1}$, have a trifle better gloss than the others. As in Group I,

when SnO_2 replaces CaO, there is a decrease in gloss, but when it replaces BaO, the gloss remains about equal.

Opacity. About same as Group I.

Pink discoloration. The pink color is about the same at cone 7 in this group as in Group I, except that some of the members of Series F (.20 eq. SnO_2) of this group were pink, while

TABLE III—MOLECULAR FORMULA, GROUP III

CONSTANT .25 KNaO, .50 Al_2O_3, 4.00 SiO_2

		SERIES G CONSTANT SnO_2=.10		SERIES H CONSTANT SnO_2=.15		SERIES I CONSTANT SnO_2=.20	
No.	ZnO	CaO	BaO	CaO	BaO	CaO	BaO
1	0	.65	0	.60	0	.55	0
2	0	.488	.162	.45	.15	.412	.137
3	0	.325	.325	.30	.30	.275	.275
4	0	.165	.488	.15	.45	.137	.412
5	0	0	.65	0	.60	0	.55
6	10	.55	0	.50	0	.45	0
7	10	.412	.137	.375	.125	.337	.112
8	10	.275	.275	.25	.25	.225	.225
9	10	.137	.412	.125	.375	.112	.337
10	10	0	.55	0	.50	0	.45
11	20	.45	0	.40	0	.35	0
12	20	.337	.112	.30	.10	.262	.087
13	20	.225	.225	.20	.20	.175	.175
14	20	.112	.337	.10	.30	.087	.262
15	20	0	.45	0	.40	0	.35
16	30	.35	0	.30	0	.25	0
17	30	.262	.087	.225	.075	....	....
18	30	.175	.175	.15	.15	.125	.125
19	30	.087	.262	.075	.225	....	....
20	30	0	.35	0	.30	0	.25

none of the members of corresponding Series C in Group I were. At cone 6, more of the members of this group are pink than in Group I. The intensity of the pink color in this group is about the same at cone 6 as at cone 7, but more of the members are pink at the lower burn.

Blistering. There was more blistering in Group II than Group I. Blistering occurs with members high in ZnO, and

of those having an equal ZnO content, there is more blistering with the high SnO_2 glazes.

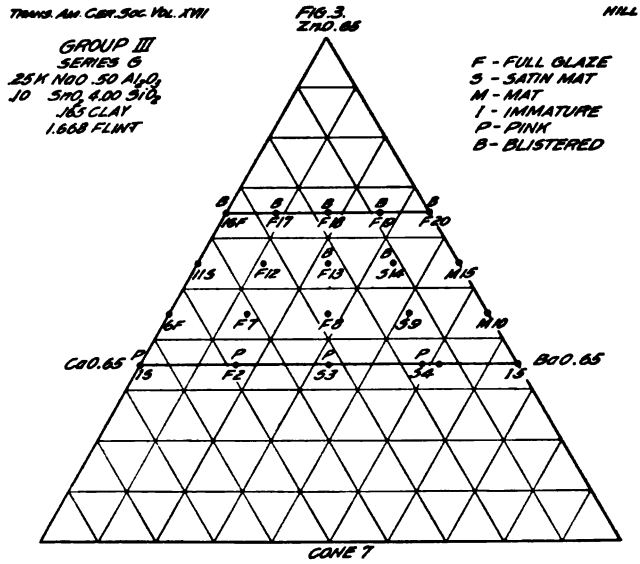
Group III. See Table III. Gloss. The gloss of this group is about the same as Group II but less than Group I. In all series, members having $\frac{CaO}{BaO} = \frac{3}{1}$ are more glossy than those with

TABLE IV—MOLECULAR FORMULA, GROUP IV

CONSTANT .20 KNaO, .325 Al_2O_3, 2.75 SiO_2

		SERIES J CONSTANT SnO_2=.10		SERIES K CONSTANT SnO_2=.15		SERIES L CONSTANT SnO_2=.20	
No.	ZnO	CaO	BaO	CaO	BaO	CaO	BaO
1	0	.70	0	.65	0	.60	0
2	0	.525	.175	.488	.162	.45	.15
3	0	.35	.35	.325	.325	.30	.30
4	0	.175	.525	.162	.488	.15	.45
5	0	0	.70	0	.65	0	.60
6	10	.60	0	.55	0	.50	0
7	10	.45	.15	.412	.137	.375	.125
8	10	.30	.30	.275	.275	.25	.25
9	10	.15	.45	.137	.412	.125	.375
10	10	0	.60	0	.55	0	.50
11	20	.50	0	.45	0	.40	0
12	20	.375	.125	.337	.112	.30	.10
13	20	.25	.25	.225	.225	.20	.20
14	20	.125	.375	.112	.337	.10	.30
15	20	0	.50	0	.45	0	.40
16	30	.40	0	.35	0	.30	0
17	30	.30	.10	.262	.087	.225	.075
18	30	.20	.20	.175	.175	.15	.15
19	30	.10	.30	.087	.262	.075	.225
20	30	0	.40	0	.35	0	.30

$\frac{CaO}{BaO} = \frac{1}{0}$. In this group, the gloss increases with any increase of ZnO in the high CaO and the high BaO glazes, but in glazes with the best gloss. $\frac{CaO}{BaO} = \frac{3}{1}$, the gloss increases with increase of ZnO up to .10 eq. only, the gloss remaining equal with further increase of ZnO.


Trans. Am. Cer. Soc. Vol. XVII
FIG. 3.
ZnO. 65
HILL
GROUP III
SERIES G
.25 K NaO .50 Al_2O_3
.10 SnO 4.00 SiO_2
.165 CLAY
1.668 FLINT
F - FULL GLAZE
S - SATIN MAT
M - MAT
I - IMMATURE
P - PINK
B - BLISTERED
CaO.65
BaO.65
CONE 7

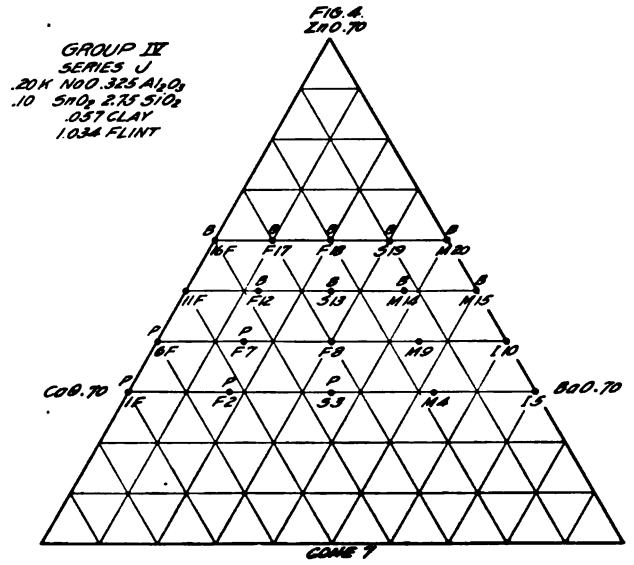


FIG. 4.
ZnO. 70
GROUP IV
SERIES J
.20 K NaO .325 Al_2O_3
.10 SnO 2.75 SiO_2
.057 CLAY
1.034 FLINT
CaO.70
BaO.70
CONE 7

Pink discoloration. The pink color is more intense and more of the members are pink than in the preceding groups. At cone 7 none of the members with .10 or more eq. of ZnO are pink, but at cone 6, the same glazes are as pink as those without ZnO. The pink color decreases with increase of SnO_2, at the

TABLE V—MOLECULAR FORMULA, GROUP V

CONSTANT .15 KNaO, .325 Al_2O_3, 2.75 SiO_2

		SERIES M CONSTANT SnO_2=.10		SERIES N CONSTANT SnO_2=.15		SERIES O CONSTANT SnO_2=.20	
No.	ZnO	CaO	BaO	CaO	BaO	CaO	BaO
1	0	.75	0	.70	0	.65	0
2	0	.562	.188	.525	.175	.488	.162
3	0	.375	.375	.35	.35	.325	.325
4	0	.188	.562	.175	.525	.162	.488
5	0	0	.75	0	.70	0	.65
6	10	.65	0	.60	0	.55	0
7	10	.488	.162	.45	.15	.412	.137
8	10	.325	.325	.30	.30	.275	.275
9	10	.162	.488	.15	.45	.137	.412
10	10	0	.65	0	.60	0	.55
11	20	.55	0	.50	0	.45	0
12	20	.412	.137	.375	.125	.337	.112
13	20	.275	.275	.25	.25	.225	.225
14	20	.137	.412	.125	.375	.112	.337
15	20	0	.55	0	.50	0	.45
16	30	.45	0	.40	0	.35	0
17	30	.337	.112	.30	.10	.262	.087
18	30	.225	.225	.20	.20	.175	.175
19	30	.112	.337	.10	.30	.087	.262
20	30	0	.45	0	.40	0	.55

expense of CaO and BaO. This difference in color is more marked at cone 6 than at cone 7.

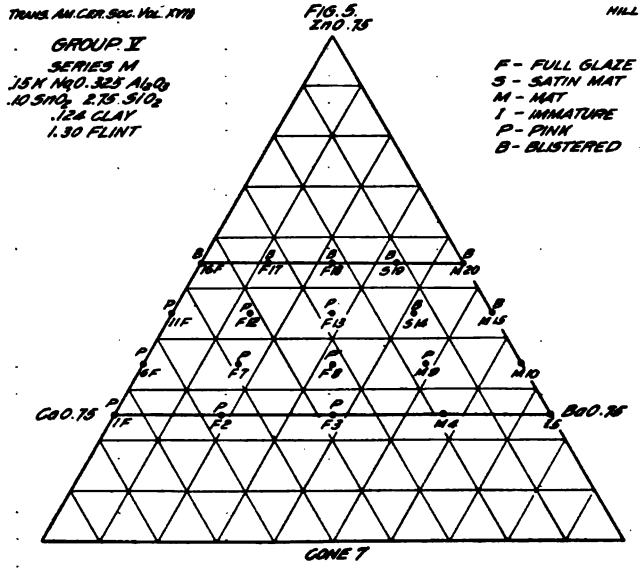
Blistering. The blistering is a trifle less than in Groups I and II.

Group IV. See Table IV. Gloss. The gloss of this group is only slightly less than Group III. The three series of the group have about the same gloss. Increase of ZnO increases the gloss in all members of the series. The glazes having the

best gloss are those with $\frac{CaO}{BaO} = \frac{3}{1}$. The glazes with high CaO are more glossy than those with equal amounts of CaO and BaO. The best mats are those with $\frac{CaO}{BaO} = \frac{1}{3}$.

Pink color. The pink in this group is considerably worse than in the preceding groups. The pink is more pronounced at cone 6 than at cone 7.

Blistering. More of the glazes are blistered than in the preceding groups.



Group V. See Table V. The gloss is a trifle less than Group IV. Gloss of the three series of the group is about the same. Increase of ZnO increases the gloss in all members of the series.

The intensity of the pink color is a trifle less than in Group IV, but more members are pink than in any other group. Some of the members with .20 eq. ZnO are pink, and they were not pink in any other groups.

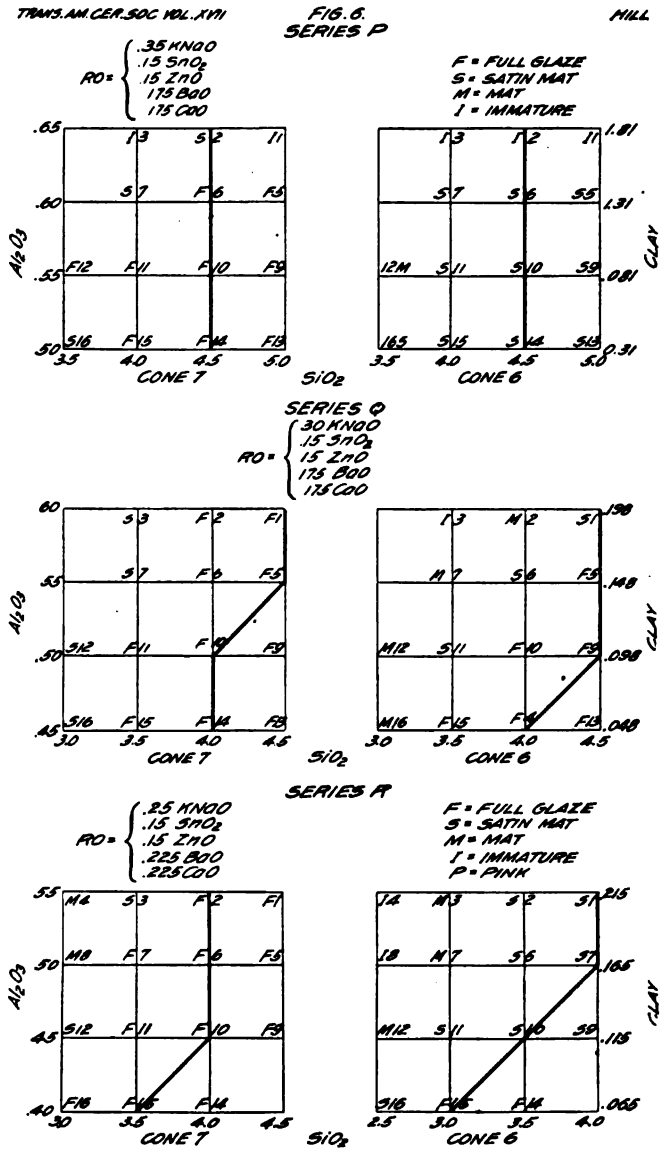
The blistering is considerably less than in Group IV.

VARIATION OF Al_2O_3—SiO_2

Five series were made with Al_2O_3-SiO_2 variations, each series having a different R O. The average of the SnO_2 and ZnO used in the R O variations was .15 eq., so the SnO_2 and ZnO were kept constant at .15 eq. each. The feldspar was varied from .35 to .15 eq., and the balance of the R O was made up of equal amounts of CaO and BaO. The formula of the glazes are given in Table VI. The results of the series are shown in Figures 6, 7 and 8. The heavy line indicates the best gloss with different Al_2O_3 contents.

TABLE VI—MOLECULAR FORMULA

	Series P		Series Q		Series R		Series S		Series T	
	R O .35 KNaO .15 SnO_2 .15 ZnO .175 CaO .175 BaO		R O .30 KNaO .15 SnO_2 .15 ZnO .20 CaO .20 BaO		R O .25 KNaO .15 SnO_2 .15 ZnO .225 CaO .225 BaO		R O .20 KNaO .15 SnO_2 .15 ZnO .25 CaO .25 BaO		R O .15 KNaO .15 SnO_2 .15 ZnO .275 CaO .275 BaO	
No.	Al_2O_3	SiO_2	Al_2O_3	SiO_2	Al_2O_3	SiO_2	Al_2O_3	SiO_2	Al_2O_3	SiO_2
1	.65	5.00	.60	4.50	.55	4.50	.50	4.00	.45	4.00
2	.65	4.50	.60	4.00	.55	4.00	.50	3.50	.45	3.50
3	.65	4.00	.60	3.50	.55	3.50	.50	3.00	.45	3.00
4	...	....	...	....	.55	3.00	.50	2.50	.45	2.50
5	.60	5.00	.55	4.50	.50	4.50	.45	4.00	.40	4.00
6	.60	4.50	.55	4.00	.50	4.00	.45	3.50	.40	3.50
7	.60	4.00	.55	3.50	.50	3.50	.45	3.00	.40	3.00
8	.60	3.50	...	....	.50	3.00	.45	2.50	.40	2.50
9	.55	5.00	.50	4.50	.45	4.50	.40	4.00	...	....
10	.55	4.50	.50	4.00	.45	4.00	.40	3.50	.35	3.50
11	.55	4.00	.50	3.50	.45	3.50	.40	3.00	.35	3.00
12	.55	3.50	.50	3.00	.45	3.00	.40	2.50	.35	2.50
13	.50	5.00	.45	4.50	...	....	.35	4.00	.35	2.00
14	.50	4.50	.45	4.00	.40	4.00	.35	3.50	...	....
15	.50	4.00	.45	3.50	.40	3.50	.35	3.00	.30	3.50
16	.50	3.50	.45	3.00	.40	3.00	.35	2.50	.30	3.00
17	...	....	...	....	...	....	...	....	.30	2.50
18	...	....	...	....	...	....	...	....	.30	2.00


TRANS. AM. CER. SOC. VOL. XVII
FIG. 6.
SERIES P
MILL
RO = .35 KNaO, .15 SnO2, .15 ZnO, .175 BaO, .175 CaO
F = FULL GLAZE
S = SATIN MAT
M = MAT
I = IMMATURE
Al2O3
CLAY
SiO2
CONE 7
CONE 6
SERIES Q
RO = .30 KNaO, .15 SnO2, .15 ZnO, .175 BaO, .175 CaO
SERIES R
RO = .25 KNaO, .15 SnO2, .15 ZnO, .225 BaO, .225 CaO
P = PINK

Results. Gloss. In all series, the glazes with the lowest Al_2O_3 content, have the best gloss. Maintaining the same Al_2O_3-SiO_2 content, the gloss decreases from Series P to T. That is, if feldspar is decreased, and clay and flint are added to keep the Al_2O_3 and SiO_2 constant, the glaze is made less glossy. But, if the clay and flint are kept constant, and the feldspar is decreased, the gloss remains about equal, or decreases only slightly, so far as we are able to judge from these formulas, as the clay and flint are not exactly the same in the different series. Also, the feldspar is being replaced by equal amounts of BaO and CaO, so that we have no direct comparison as to the effect of the different amounts of feldspar on the gloss.

Whiteness and opacity. The glazes with the best gloss are the whitest in color. Since Al_2O_3 decreases the gloss in these series, it likewise decreases the whiteness. This is due in part to the fact, that ball clay has a buffish color, and the high clay glazes are more buff in tone than the others.

Pink color. None of the glazes were pink at cone 7. At cone 6 in Series S and T, members having the two lowest clay contents were pink, and of these, the more intense color occurred with the lower SiO_2 contents. That pink color was developed in these two series and not in the others, must be due to the increased CaO and BaO in Series S and T, but it is not evident why the pink color occurred only with the lower Al_2O_3 contents.

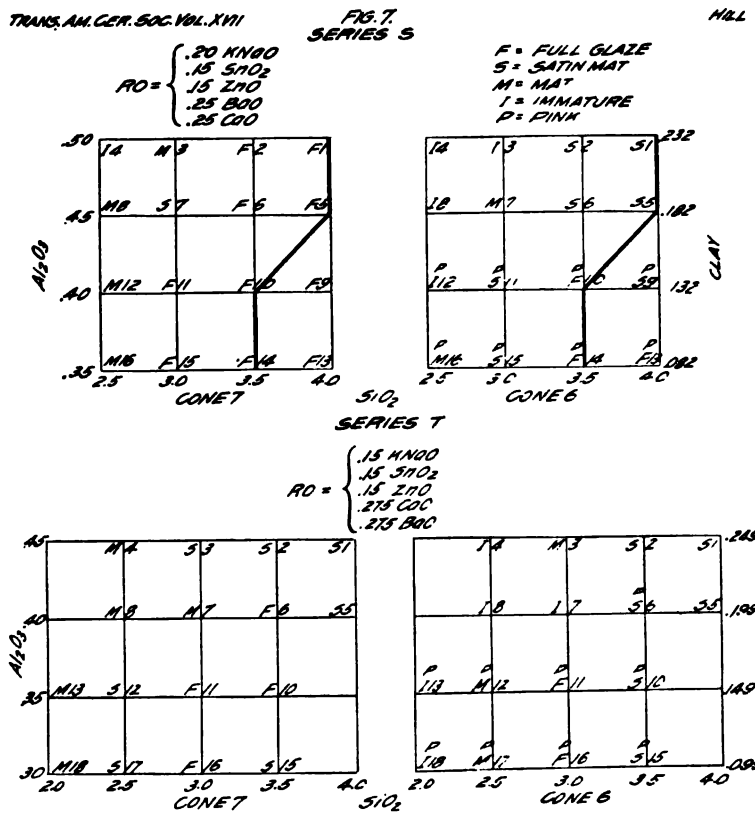
Blistering. There was no blistering in any of the series of the Al_2O_3-SiO_2 variations.

SUMMARY

Gloss. CaO seems to be essential for this type of glaze. Since CaO reacts with both clay and flint, the amount to be used to produce maximum gloss depends upon the clay and flint present, and since the latter vary in the different groups, no limits for CaO can be set down from these series. If the glaze is overloaded with CaO, the excess CaO decreases the gloss, so that if ZnO be substituted or small amounts of BaO, the gloss is increased. If the CaO is high, then increases of ZnO up to .30 eq. increase the gloss in these experiments. But if the amount of

CaO present is less than that required for maximum gloss, then additions of ZnO up to .10 eq. increase the gloss, but with further additions, the gloss remains about equal.

Since the more complex R O gives the more fusible glaze, and since ZnO reacts with SiO_2 readily, it is evident why con-



siderable amounts of ZnO can replace CaO without decreasing the fusibility. From these experiments, it seems that at least half of the CaO required for maximum gloss can be replaced by ZnO. When less than the maximum amount of CaO or ZnO or mixtures of both necessary to produce the highest gloss, are present in the glaze, BaO from barium carbonate decreases the

gloss. But when the CaO and ZnO are present in more than the maximum amount, substituting BaO for either CaO or ZnO will increase the gloss, since it replaces excess CaO or ZnO and since it is making the R O more complex. This is why we find in some of the groups that a ratio of $\frac{CaO}{BaO}=\frac{3}{1}$ gives a more glossy glaze than $\frac{CaO}{BaO}=\frac{1}{0}$, and this holds true as ZnO replaces both in the same ratio. The gloss is less when $\frac{CaO}{BaO}=\frac{1}{1}$, and any further increase of BaO rapidly decreases the gloss.

When SnO_2 replaces CaO or ZnO, the gloss is diminished, but when it replaces BaO, the gloss remains about the same.

In these experiments, when the KNaO from feldspar is replaced by equal amounts of CaO and BaO, the gloss remains equal, or decreases only slightly. Had KNaO been replaced by CaO alone, the gloss would probably remain the same, but if replaced by BaO the gloss would have been diminished.

Regardless of the amounts of SiO_2 and feldspar present, the best gloss and the most fusible glazes were obtained in these experiments with the lowest clay contents. The lowest clay used in this study was .031 eq. in Series P.

The best gloss was found in these series when the Al_2O_3-SiO_2 was from 1:8 to 1:10, the lower feldspar glazes requiring the higher ratios for maximum gloss.

Whiteness and Opacity. Increase of SnO_2 at the expense of CaO, BaO or ZnO, increases the whiteness. The effect of SnO_2 on the whiteness decreases as the amounts of SnO_2 are increased. Increase of ZnO makes the glaze whiter, but its effect is much less than that of SnO_2.

Where the gloss remains equal, there is no difference in the whiteness when BaO replaces CaO up to equal equivalents of each. As the BaO is increased, the glaze is made considerably whiter, but the gloss is greatly diminished. The different amounts of feldspar here used did not make any difference in the color.

Additions of Al_2O_3 decreased the whiteness of these glazes, since the ball clay tends to give a buffish tint to the glaze.

Pink Discoloration. The development of a decided pink color in glazes containing SnO_2 is quite common. It was mentioned by Albery, Vol. XIV, *Trans. Amer. Cer. Soc.* By replacing part of the CaO in the enamel with PbO, MgO and ZnO, the tendency to pink was overcome. While the pink is due to glaze composition, it is influenced by the temperature of firing and the atmosphere of the kiln. The results of the burns checked much better than had been anticipated, though quite a few of the glazes marked pink on the charts were pink in one kiln and not in the other, fired at approximately the same temperature. The color produced varies from a faint pink blush to a color equal to that produced by light pink chrome-tin stains.

The members of the different series that were pink increased from Group I to Group V, where the KNaO is being replaced by CaO and BaO. Series C, Group I, is the only series out of the five groups in which none of the members were pink, and this series is the lowest in CaO and BaO. Series M, Group V, had more of the members pink than any other, and this series is highest in CaO and BaO.

None of the members of Group I were pink that contained ZnO, and in Group V, none of the members with .30 eq. ZnO were pink. In all series, when the $\frac{CaO}{BaO}$ ratio is kept constant, an increase of ZnO tends to overcome the pink color.

None of the glazes that did not contain CaO were pink—so that the pink color seems to be due to some lime-tin combination. But the glazes that were highest in CaO and SnO_2 were not the deepest in color. In Group I, where the least pink occurred, the glazes that were pink did not contain ZnO and had a $\frac{CaO}{BaO}$ ratio of from $\frac{1}{0}$ to $\frac{1}{1}$. The intensity of the color increased from the former to the latter, but further additions of BaO did not produce a pink color. In all the series, when there was no ZnO in

the glaze the intensity of color increased as in Group I above, but, in the series having more of the members pink, the glaze having $\frac{CaO}{BaO}=\frac{1}{3}$ was also pink, but not so pink as the ones with higher CaO.

In the series that were pink with ZnO in the glaze, the members that had the most intense color were not those with $\frac{CaO}{BaO}=\frac{1}{1}$, as was the case when no ZnO was present, but those that had a higher $\frac{CaO}{BaO}$ ratio. This was true of all series except a few at cone 6, where the members with .10 ZnO were as deep in color as those that did not contain ZnO.

A substitution of SnO_2 for CaO and BaO in all groups decreased the pink color, both in intensity and in the members of the series that were pink. This shows that only a small amount of SnO_2 is necessary to produce the pink color, and that an increase of SnO_2 will generally lessen the chances of pink color being formed rather than increase them.

More of the members were pink at cone 6 than at cone 7, so that a decrease in the firing temperature may cause pink to be formed with a glaze that is free from pink at higher temperatures. But at the same time, many of the members had a more intense color at cone 7 than at cone 6. In general, it was found that the groups that did not have many of the members pink, had a greater intensity of color at cone 6, but the groups that had a larger number of the members pink, had a more intense color at cone 7.

There is no relation between the gloss of the trials and the intensity of the pink color, for generally the trials had considerably more gloss at cone 7 than at cone 6, and, as mentioned above, many of the trials were more pink at the lower heat. Some of the trials at cone 6 were dull and immature, yet had a deep color.

In the series of the Al_2O_3-SiO_2 variations, there was no pink at cone 7. At cone 6, there was pink formed in the two series

highest in CaO and BaO. The pink members were those lowest in Al_2O_3.

To summarize, the pink color is caused by a combination of tin and lime, this combination being low in tin and comparatively high in lime. (Glazes of same composition as those used in this study, but not containing SnO_2, do not develop pink color). The tendency to pink may be overcome by substituting KNaO or ZnO for CaO. A substitution of BaO for CaO will probably not decrease the tendency to pink unless the glaze already contains equal equivalents of each.

Blistering. None of the glazes were blistered at cone 6. At cone 7, all of the glazes that contained .3 eq. ZnO were blistered. Of those containing .20 eq. ZnO, those high in BaO were blistered more than those high in CaO. When SnO_2 was substituted for CaO and BaO, the blistering was increased. None of the glazes containing .10 eq. ZnO were blistered, and none were blistered in the Al_2O_3-SiO_2 variations, where ZnO was kept constant at .15 eq. Group IV (.20 eq. feldspar) had more blistering than the other groups, and Group V had more than Groups I-III (.35-.25 eq. feldspar). Group III had the least blistering.

Blistering is due to the volatilization of ZnO or some zinc compound in the glaze. The percent by weight of zinc oxide in the batch formula is about the same for the same equivalent ZnO in Group IV and V, and is about 1¼ percent higher than for Groups I-III which have about the same weight of zinc oxide for the same equivalent ZnO. This difference may account for the increased blistering in Groups IV or V. Or it may be due to the ability of the high feldspar glazes to hold the ZnO free from volatilization, as stated by Purdy (Vol. XIII, p. 578), but does not show a regular gradation in these groups, because the clay and flint are different with the different feldspar content in the various groups.

CONCLUSION

The results of this study agree in general with what has already been published on Bristol and terra-cotta glazes, even though the R O is more complex, and the limits of composition are considerably different. There is, however, one point which

seemingly does not agree with what has been published and which might be well to mention.

Regarding the effect of clay on fusibility, in Vol. V, p. 159, Purdy gives evidence that shows that a considerable amount of clay must be added to Bristol glazes to get the maximum fusibility. The cases where the highest amount of clay is added to a glaze containing no clay, are given below:

$$\text{I} \quad \left.\begin{matrix} .20\ K_2O \\ .40\ CaO \\ .40\ ZnO \end{matrix}\right\} .20\ Al_2O_3 \left\{ 1.20\ SnO_2 \right.$$

The maximum fusibility was not reached by adding clay up to .20 eq. to this glaze containing no clay.

$$\text{II} \quad \left.\begin{matrix} .25\ K_2O \\ .35\ CaO \\ .40\ ZnO \end{matrix}\right\} .25\ Al_2O_3 \left\{ 1.50\ SiO_2 \right.$$

Maximum fusibility was reached by adding .12 eq. clay, and .24 eq. clay were added without decreasing the fusibility of the glaze.

In the Al_2O_3-SiO_2 variations of this study, regardless of flint and feldspar, any increase of clay decreased the gloss and fusibility of the glazes. The lower limit of clay in these series was .031 eq. in Series P and an increase of .05 eq. clay decreased the fusibility of the glaze. At cone 6, Nos. 13-16, (.031 eq. clay) were well matured and formed a smooth glaze of fair gloss, while Nos. 9-12 (.081 eq. clay) were much less matured and had a rough surface with less gloss.

The effect of clay on the gloss was the same in the other series, but the lower limits of clay were somewhat higher.

Allowing for the fact that Purdy calculated the Mayfield ball clay as pure clay substance, equivalent weight, 258, while the ball clay used here was calculated as 70.25 percent clay substance, and that the CaO and ZnO in these series, was lower than that used by Purdy, it is not evident why so much clay could be added to the Bristol glazes without decreasing the fusibility.

DISCUSSION

Mr. Purdy: It is impossible to compare this series with the series of Bristol glaze in Volume V to which he referred, on account of the difference in the R O. I had a larger content of CaO, and in addition thereto, a very low content of SiO_2. Our maximum ratio of silica to alumina was 5½ to 1, whereas he has his quite high, running as high as 10. That gives less opportunity for the calcium to react with the clay, because the calcium will go with the silica in preference. And then too, having higher calcium in the Volume V series of Bristol glazes, we had a greater opportunity to take care of the clay. It could be shown, on the basis of norms, that additions of clay in that series increased the fusibility, even though we had not the direct evidence of the cones and of the glazes. The series of stoneware glazes reported in Volume V have been repeated in commercial kilns under practical stoneware conditions, time and time again. Reports have been published in the *Transactions* checking these findings, that is, in the Bristol glazes, having high CaO and 4 ZnO, we can increase the clay up to a given point with each feldspar content and obtain increased fusibility. There are plenty of reasons why Mr. Hill did not find it so with his R O which had very low calcium content and high barium, and also high silica. There is no parallelism or discrepancy between the two studies so far as I can see.

Mr. Hill: Professor Purdy speaks of the high ratio of Al_2O_3 to SiO_2. In the Al_2O_3-SiO_2 variations, the ratio of Al_2O_3 to SiO_2 is as low as 6.7. The CaO and BaO in the different R O increases with decrease of feldspar, so that with .15 eq. feldspar in the last series, I have .275 BaO and .275 CaO, but the lowest clay in this series is .099 eq. In the first series, where I had the lowest clay, .031 eq. the CaO and BaO is only .175 eq. each.

I wish to point out the fact that where the ZnO and CaO are low as in this study, a high clay content decreases the fusibility, which is contrary to what I had learned about stoneware glazes. My experience has been that you get the brightest and most fusible glaze with the lower clay contents, but with high CaO and high ZnO, the conditions are different.

Mr. Purdy: He was judging his fusibility by the appearance of the glaze. He has R O oxides that would tend to give him surface phenomena that would make it difficult to judge comparative fusibility by such means. The fusibility of the glazes reported in Volume V, were by cones as well as by the appearance of the glaze. If you obtain a mat you would think you had a refractory glaze, whereas it may not be. He might have thought he had and not had, or he might have have a refractory glaze and not have known it.

Then, too, his series is not really a Bristol glaze series.

Mr. Watts: In my study, which also is really not a Bristol glaze, the ratio of alumina to silica down in the anorthite corner is one to two, and there is no alumina present in the other calcium combination; however the figures showed that in the combination of feldspar, wollastonite and willemite, the formula stands 0.125 Al_2O_3—1.25 SiO_2. That of course is very low alumina and silica. Anorthite, synthetically prepared, consists of one molecule of calcium oxide and one molecule of clay, so there you get the clay in the anorthite in this series. In order to make the most fusible mixture, you should have 50 percent of feldspar, 12½ percent of anorthite and 27½ percent of willemite. That gives you 0.15 K_2O—0.25 CaO and 0.375 ZnO—0.625 Al_2O_3 and 3.438 SiO_2 That was the most fusible mixture of this second series. I am going to lay the trials out, so that any of you that want to judge of these fusions or degrees of fusibility can do so for yourself. All of the trials I made were stood on edge in the kiln, so that there was a chance for the glaze to flow if there was any disposition to flow, and that tendency is evidenced in some of the trials. The trials seem to bear out the statement, that you have to keep your clay reasonably low unless your lime is high. But where the lime is high, at least at cones 4, 6 and 8, within the range of the investigation I conducted, I do not find that high lime and high clay gives you as fusible a mixture as where you keep your lime lower and introduce your alumina practically all from feldspar, and very little of it from clay.

Mr. Purdy: Was your total alkali five tenths?

Mr. Watts: Yes, that gives you 0.125 clay.

Mr. Purdy: That 0.125 equivalents of clay, which is very high indeed for that feldspar content, gave the most fusible glaze in the series. In that particular case, the clay certainly did increase the fusibility of the mixture.

Mr. Watts: It did not, because if you will refer to the same member in the other series you will find where I had no clay at all, the alumina being .125, all from feldspar, the glaze was more fusible.

Mr. Purdy: The point I make is, that with that R O, you got your most fusible glaze with the alumina 0.625. If the clay had been left out altogether, you would not have had as fusible a mixture.

Mr. Watts: So far as that is concerned, this was the limit of the series in which the lime was not introduced at all. The other end of the series consisted merely of feldspar and willemite. This was the lowest content of lime and necessarily the lowest content of clay which it was possible to introduce in a series of this sort unless I had made the series with more members.

Mr. Bleininger: I was very much interested in the question of the pink color produced in glazes of this sort. The same phenomenon occurs in low-fire tin enamels and I wonder whether the custom practiced in Europe of mixing the frit with salt in order to vaporize any iron salts that may be there, is associated with the question of the pink color in tin enamels? It is a fact that the lime tends to produce the pink color. I simply want to offer as a further suggestion the possibility of iron compounds being formed.

Prof. Parmelee: Several oxides readily change their state of oxidation, among these is tin. Advantage is taken of this fact in the production of copper reds. According to Seger, the tin oxide is used in that case as an oxidizing agent, changing from the stannic oxide to the stannous oxide. Is it possible, that in the glazes that have blistered, the stannic oxide has changed to stannous oxide liberating some oxygen and giving rise to the formation of blisters? We have similar examples in the oxides of manganese and cobalt.

Mr. Stover: This tin is employed in the endeavor to get a white, opaque glaze; and the tin is what you don't want. I had at the Boston meeting, 12 years ago, some 1200 and odd samples to show that the potters, who said the underglazed tin-pink could not be made in America because we fired too high, were mistaken. I produced 1200 odd trials, at all the various heats I could find in Trenton and running up as high as cone 12, all of which showed quite clearly tin pink. In that case I was trying to get it. In this case they are trying to get rid of it.

DISCUSSION WRITTEN AFTER PAPER WAS DISCUSSED

Mr. Hill: Regarding the effect of the clay on fusibility of Bristol glazes: In Vol. V, pages 150 and 151, Prof. Purdy gives the deformation temperature of the glazes without clay, and with the amount that was added to get the greatest fusibility, as follows:

No.	CaO	ZnO	K_2O	Al_2O_3	SiO_2	CLAY EQ.	FLINT EQ.	FUSION TEMP.
I A	.4	.4	.2	.2	1.2	.0	.0	1150°
I H	.4	.4	.2	.4	2.2	.2	.6	1075°
11 A	.35	.4	.25	.25	1.5	.0	.0	1125°
11 G	.35	.4	.25	.45	2.47	.2	.57	1115°

The increased fusibility of 1 H over 1 A and 11G over 11 A, Prof. Purdy states is due to the increase of clay. It is a well known fact, that free flint added to a glaze of this type containing no flint, will result in a more fusible glaze, so that a part of the increased fusibility is due to the increased flint.

In Vol. XIII, page 550, "Porcelain Glazes," the results of a series of glazes are given. The limits of the formula are:

$$\left.\begin{matrix}.0—.8\ CaO\\ .0—.8\ ZnO\\ .2—.5\ K_2O\end{matrix}\right\} .50—.80\ Al_2O_3 \left\{ 3.0—4.8\ SiO_2\right.$$

The ratio of Al_2O_3 to SiO_2 is kept constant at 1:6.

On page 579, basing his predicitions on the results given in Vol. V, he says: "Comparing the extremes of the series, it is noted that within any group, increase of clay decreases the fusibility of the mixtures. In group 1 (.2 eq. K_2O) we probably

started (according to Purdy's curves, p. 158, Vol. V) with the most fusible mixtures and added clay to them, while in the other groups, we started with mixtures which had already been made less fusible by addition of clay, hence we should expect to have increased refractoriness. A decrease of clay in Group 1, from 3 eq. to 0 eq. would no doubt have likewise decreased the fusibility of the glazes of this group."

TABLE VII—SERIES B—RO=0.6 CaO, 0.2 ZnO, 0.2 K_2O

No.	Al_2O_3	SiO_2	CLAY EQ.	FLINT EQ.	TIME OF DEFORMATION 1ST BURN	TIME OF DEFORMATION 2ND BURN
1 B 6	.50	3.00	.30	1.20	(1) 5:50 P. M. (2) 6:00 P. M.	(1) 4:30 A. M. (2) 4:40 A. M.
1 B 7	.40	2.40	.20	.80		(1) 9:00 A. M. (2) 9:15 A. M.
1 B 8	.30	1.80	.10	.40		(1) 1:30 P. M. (2) 1:30 P. M.
1 B 9	.25	1.50	.05	.20		(1) 2:40 P. M. (2) 3:00 P. M.
1 B 10	.20	1.20	0	0		(1) 8:15 P. M. (2) 8:00 P. M.
1 B 7X	.40	2.80	.20	1.20	(1) 7:30 P. M. (2) 7:45 P. M.	(1) 6:50 A. M. (2) 7:00 A. M.
1 B 8X	.30	2.60	.10	1.20		(1) 12:55 P. M. (2) 12:55 P. M.
1 B 9X	.25	2.50	.05	1.20		(1) 1:05 P. M. (2) 1:25 P. M.
1 B 10X	.20	2.40	0	1.20		(1) 2:15 P. M. (2) 2:15 P. M.

1st Burn: Cone 04—12:30 P. M. Cone 1—7:30 P. M.

2nd Burn: Cone 04—4:15 A. M.; Cone 1—7:15 A. M.; Cone 2—9:30 A. M.; Cone 3—1:30 P. M.; Cone 4—3:00 P. M.; Cone 6—8:00 P. M.

Glaze 1 B 6, high clay, is the most fusible of the series, and glazes with next higher clay are next in order of fusibility. Glaze 1 B 6 went down 15½ hours before 1 B 10. (No clay or flint.)

The lowest clay content in Group 1 was .30 eq. Since the series did not contain any glazes with clay lower than .30 eq., it was decided to make up the same mixtures and decrease the clay, as it was thought that some mixtures with clay lower than .30 eq. would be found that were more fusible than those with .30 eq. Accordingly, the glazes in Group 1, Series B, C and D (see p. 554, Vol. XIII) were made, but with clay decreasing from .30 eq. maintaining the ratio of Al_2O_3 to SiO_2 as 1:6. The same glazes were also made with clay decreasing, but with SiO_2 remaining the same throughout.

The materials used were the same as those used by Prof. Purdy, Brandywine feldspar, Mayfield ball clay, flint, whiting and zinc oxide; 500 grams of each glaze was weighed up, blunged with water for 30 minutes in small jar mills, dried, and cones made from each mixture. Two cones of each mixture in the same series were placed on a clay slab 15 inches long. The three slabs containing the cones of the three series were placed in the kiln, one above the other, so that all were the same distance from the muffle, and so that all would receive as near the same heat treatment as possible. The first burn was made in a 6 ft. muffle test kiln, with peep holes placed in the door so that all of the cones could be seen at the same time. The kiln was fired to cone 2, but it was necessary to take the kiln off before all the cones were down. The second burn was made in a 15 ft. muffle kiln, fired to cone 7. No pyrometer equipment was available at this time, but the time of deformations of the cones was taken, giving the order of their fusibility.

The formula of the glazes and the time of deformation are shown in Tables VII, VIII and IX.

Summary of Results on Group 1 (.2 K_2O). Series B—.6 CaO, .2 ZnO. The glaze with the highest clay (.30 eq.) is the most fusible one, whether the free SiO_2 decreases with the clay, or remains constant.

Series C—.4 CaO, .4 ZnO. The glaze with the highest clay is the most refractory one of the series. When the Al_2O_3—SiO_2 ratio remains at 1:6, the glaze with .20 clay is more fusible than any containing less clay. But if the SiO_2 remains the same, and

only the clay is decreased, the most fusible glaze is the one with .10 eq. clay, and the next one in order of fusibility contains .05 eq. These two glazes are the most fusible ones of the entire group.

Series D—.2 CaO, .6 ZnO. The glaze with no clay is the most fusible one, either with SiO_2 remaining constant or with SiO_2 decreasing with the clay.

TABLE VIII—SERIES C—RO=0.4 CaO, 0.4 ZnO, 0.2 K_2O

No.	Al_2O_3	SiO_2	CLAY EQ.	FLINT EQ.	TIME OF DEFORMATION 1ST BURN	2ND BURN
1 C 6	.50	3.00	.30	1.20	(1) 7:30 P. M. (2) 7:50 P. M.	(1) 10:30 A. M. (2) 10:30 A. M.
1 C 7	.40	2.40	.20	.80	(1) 3:30 P. M. (2) 3:35 P. M.	(1) 2:15 A. M. (2) 2:20 A. M.
1 C 8	.30	1.80	.10	.40	(1) 4:30 P. M. (2) 4:45 P. M.	(1) 3:00 A. M. (2) 3:00 A. M.
1 C 9	.25	1.50	.05	.20	(1) 4:50 P. M. (2) 5:00 P. M.	(1) 3:45 A. M. (2) 3:50 A. M.
1 C 10	.20	1.20	0	0	(1) 5:00 P. M. (2) 5:15 P. M.	(1) 6:00 A. M. (2) 6:30 A. M.
1 C 7X	.40	2.80	.20	1.20	(1) 3:20 P. M. (2) 3:25 P. M.	(1) 2:15 A. M. (2) 2:45 A. M.
1 C 8X	.30	2.60	.10	1.20	(1) 2:20 P. M. (2) 2:30 P. M.	(1) 1:45 A. M. (2) 1:50 A. M.
1 C 9X	.25	2.50	.05	1.20	(1) 2:35 P. M. (2) 2:50 P. M.	(1) 2:00 A. M. (2) 2:10 A. M.
1 C 10X	.20	2.40	0	1.20	(1) 4:00 P. M. (2) 4:40 P. M.	(1) 2:50 A. M. (2) 3:00 A. M.

1st Burn: Cone 04—12:30 P. M. Cone 1—7:30 P. M.

2nd Burn: Cone 04—4:15 A. M.; Cone 1—7:15 A. M.; Cone 2—9:30 A. M.; Cone 3—1:30 P. M.; Cone 4—3:00 P. M.; Cone 6—8:00 P. M.

Glaze 1 C 6 with the highest clay is the most refractory of the series. 1 C 7, .20 eq. clay is the most fusible glaze with Al_2O_3 to SiO_2 as 1:6, but is more refractory than 1 C 8X and 1 C 9X, with clay .10 and .05 eq., SiO_2 constant.

Prof. Purdy has shown, regarding Bristol glazes: (1) That, with .2 K_2O as the lower limit as the feldspar is increased, the amount of clay must be decreased to maintain equal fusibility. (Vol. V.)

(2) That any increase of clay above .30 eq. will make the glaze more refractory, Vol. XIII.

(3) That .4 eq. feldspar gives the most fusible glaze (Vol. V).

TABLE IX—SERIES D—RO=0.2 CaO, 0.6 ZnO, 0.2 K_2O

No.	Al_2O_3	SiO_2	CLAY EQ.	FLINT EQ.	TIME OF DEFORMATION	
					1ST BURN	2ND BURN
1 D 6	.50	3.00	.30	1.20		(1) 1:30 P. M. (2) 1:30 P. M.
1 D 7	.40	2.40	.20	.80		(1) 1:45 P. M. (2) 1:45 P. M.
1 D 8	.30	1.80	.10	.40		(1) 10:30 A. M. (2) 11:00 A. M.
1 D 9	.25	1.50	.05	.20	(1) 7:15 P. M. (2) 7:30 P. M.	(1) 4:45 A. M. (2) 4:55 A. M.
1 D 10	.20	1.20	0	0	(1) 7:45 P. M. (2) 7:45 P. M.	(1) 4:55 A. M. (2) 5:15 A. M.
1 D 7X	.40	2.80	.20	1.20		(1) 2:00 P. M. (2) 2:00 P. M.
1 D 8X	.30	2.60	.10	1.20	(1) 8:00 P. M.	(1) 7:10 A. M. (2) 7:10 A. M.
1 D 9X	.25	2.50	.05	1.20	(1) 6:00 P. M. (2) 6:15 P. M.	(1) 3:00 A. M. (2) 3:00 A. M.
1 D 10X	.20	2.40	0	1.20	(1) 4:25 P. M. (2) 5:00 P. M.	(1) 2:50 A. M. (2) 2:55 A. M.

1st Burn: Cone 04—12:30 P. M. Cone 1—7:30 P. M.

2nd Burn: Cone 04—4:15 A. M.; Cone 1—7:15 A. M.; Cone 2—9:30 A. M.; Cone 3—1:30 P. M.; Cone 4—3:00 P. M.; Cone 6—8:00 A. M.

1 D 10X, no clay, is most fusible glaze of this series.

The results of the glazes cited above show that with .2 K_2O, the most fusible glazes were in Series C, having equal equiva-

lents of CaO and ZnO, and that in this series, the most fusible glazes contained .10 and .05 eq. clay. Now, with .2 eq. feldspar, the most fusible glazes contain .10 eq. or less clay, and since an increase of feldspar to .4 eq. would increase the fusibility, and the glaze must contain less clay with the higher feldspar contents to have equal fusibility, it is evident that the most fusible mixture of the components of Bristol glaze must contain less than .10 eq. clay.

In conclusion, regarding the assumption of Purdy, p. 579, Vol. XIII, "In Groups I and II, (.20 and .25 eq. K_2O) we probably started (according to Purdy's curves, Vol. V, p. 158) with the most fusible mixture and added clay to them,—". The mixtures referred to contained .30 eq. clay, so that the mixture is the most fusible one, only when the ratio CaO to ZnO is 3 to 1 or greater. The statement "A decrease of clay. in Group 1 from .3 eq. to 0 eq. would no doubt have likewise decreased the fusibility of the glazes of this group" is not true when the ratio of CaO to ZnO is 1:3 or less.

THE EFFECT OF GROG IN A FIRE CLAY BODY

BY C. E. FULTON AND R. J. MONTGOMERY

In the manufacture of refractory bodies, it is an almost universal practice to introduce part of the fire clay in a burned condition—that is, as grog. It is generally recognized that the chief function of grog is to decrease both the drying and burning-shrinkage and to increase the porosity of the burned ware. The purpose of this paper is to show the effect of the amount, and of the size of the grog, upon a typical fire-clay body.

The data here given were obtained upon bodies made from St. Louis fire clay. The raw clay was ground to pass a twenty mesh screen. The grog was obtained by burning the raw clay to about cone 6 and crushing it to the desired size.

Details of Experiment. This work is divided into two sections. The effect of the amount of grog is shown by the members of Series A, and the effect of the size of the grog by the members of Series B.

Series A.—Effect of Amount of Grog. This series contains four members:

(1) 0 percent grog, 100 percent raw clay.
(2) 25 percent grog, 75 percent raw clay.
(3) 50 percent grog, 50 percent raw clay.
(4) 75 percent grog, 25 percent raw clay.

The grog was crushed to pass a ten mesh screen. A sieve test gave the following residues on Tyler Standard Screen Scale testing sieves:

10.4	percent on	14-mesh
31.8	percent on	28-mesh
18.6	percent on	65-mesh
16.8	percent on	150-mesh
22.4	percent through	150-mesh

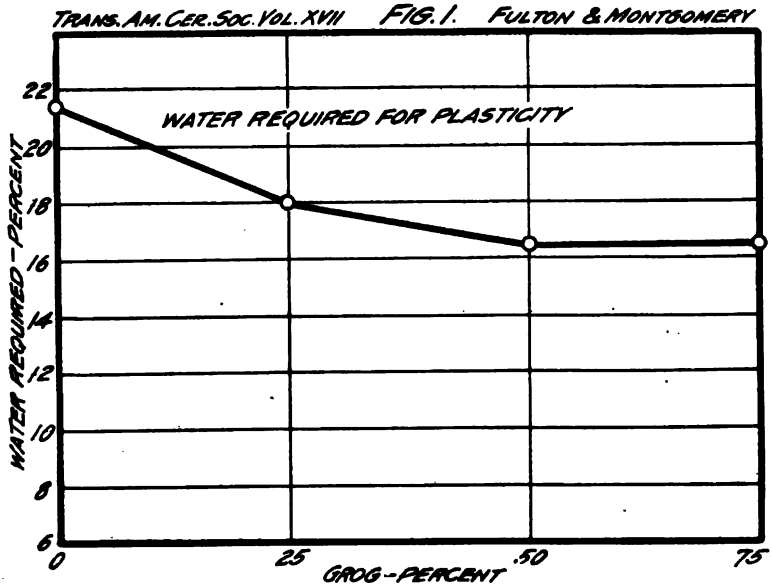
Series B.—Effect of Size of Grog. In this series, the object is to show the effect of the size of grog in a body containing 50 percent raw clay and 50 percent grog. Five different sizes of

TABLE I—SERIES A—EFFECT OF AMOUNT OF GROG

	1	2	3	4	
Grog, percent	0	25	50	75	
Water for plasticity	21.5	18.0	16.5	16.5	Fig. 1
Linear drying shrinkage	7.7	5.8	4.4	1.9	Fig. 2
Modulus of rupture, raw	723	417	220	80	Fig. 3
Burning shrinkage—					
cone 010	2.4	1.0	0.2	0.1	
cone 5	6.0	3.0	1.2	0.3	
cone 10	7.2	3.9	2.2	1.3	Fig. 4
cone 15	6.9	5.3	4.1	3.5	
cone 20	4.2	4.8	4.0	3.4	
Modulus of rupture—					
cone 010	1500	1162	538	351	
cone 5	3193	2212	1016	570	
cone 10	4753	2636	1208	697	Fig. 5
cone 15	3033	3485	2307	2080	
cone 20	2111	3780	2678	2613	
Apparent specific gravity—					
cone 010	2.56	2.70	2.68	2.68	
cone 5	2.51	2.67	2.68	2.66	
cone 10	2.40	2.61	2.62	2.61	Fig. 6
cone 15	2.35	2.43	2.51	2.52	
cone 20	2.24	2.38	2.40	2.40	
Apparent porosity—					
cone 010	22.3	28.7	29.7	33.5	
cone 5	10.3	23.7	28.4	32.5	
cone 10	2.3	19.1	23.7	28.9	Fig. 7
cone 15	3.1	10.6	14.1	21.4	
cone 20	9.4	10.5	11.1	13.2	

grog were used. These sizes were obtained by crushing the burned clay to pass the desired screen, care being taken to keep the material passing through as coarse as possible. All the material passing the screen was used. The various sizes were obtained with the following Tyler Standard sieves:

(1) 6-mesh—size of hole 0.131 inches.
(2) 14-mesh—size of hole 0.046 inches.
(3) 35-mesh—size of hole 0.0164 inches.
(4) 100-mesh—size of hole 0.0058 inches.
(5) 200-mesh—size of hole 0.0029 inches.



Tests Made. The tests made on Series A and B were:

1. Water required to develop plasticity.
2. Linear drying shrinkage.
3. Modulus of rupture—unburned body.
4. Burning shrinkage—bodies burned to various cones.
5. Modulus of rupture—bodies burned to various cones.
6. Apparent specific gravity—bodies burned to various cones.
7. Apparent porosity—bodies burned to various cones.

TABLE II—SERIES B—EFFECT OF SIZE OF GROG

	1	2	3	4	5	
Mesh	6	14	35	100	150	
Water for plasticity	16.8	17.2	18.2	20.7	21.8	Fig. 8
Drying shrinkage	4.2	4.7	5.1	5.8	6.3	Fig. 9
Modulus of rupture, raw	238	335	386	495	358	Fig. 10
Burning shrinkage—						
cone 010	0.5	0.2	0.8	0.7	0.6	
cone 5	1.5	1.6	1.2	1.6	2.2	
cone 10	2.2	2.3	2.3	3.3	2.7	Fig. 11
cone 15	4.9	5.1	5.2	7.6	8.7	
cone 20	5.0	5.6	5.5	7.2	7.4	
Modulus of rupture—						
cone 010	572	1043	1166	1497	1284	
cone 5	1209	2005	2410	3387	3125	
cone 10	1335	2280	3020	3537	3822	Fig. 12
cone 15	2528	4317	5538	6080	6622	
cone 20	2860	3857	5260	5220	4187	
Apparent specific gravity—						
cone 010	2.68	2.68	2.66	2.68	2.70	
cone 5	2.68	2.68	2.66	2.67	2.69	
cone 10	2.64	2.65	2.62	2.65	2.64	Fig. 13
cone 15	2.52	2.52	2.52	2.46	2.47	
cone 20	2.47	2.46	2.34	2.38	2.39	
Apparent porosity—						
cone 010	29.6	29.0	29.0	32.6	34.3	
cone 5	27.6	26.8	27.6	30.4	31.8	
cone 10	24.7	23.7	24.6	27.7	25.7	Fig. 14
cone 15	13.2	10.5	10.3	5.8	4.7	
cone 20	10.8	7.2	2.4	4.4	6.4	

Figures 1 to 7 inclusive show in graphic form the effect of the amount of grog, and figures 8 to 14 inclusive show the effect of the fineness of grog.

In making these tests, three separate burns were made at each temperature to insure correct results. The bars from each burn were tested, and the data in Tables I and II are the averages of the three burns. Details of the testing methods used are given in another contribution from this laboratory, published in this volume, and entitled "Laboratory Methods for the Physical Testing of Fire Clays."

Discussion of Curves.

Series A.—Effect of the Amount of Grog.

Figure 1. The water required to develop plasticity decreases as the grog is increased.

Figure 2. The addition of grog decreases the linear drying shrinkage.

Figure 3. The strength of the unburned body is decreased markedly by the addition of grog.

Figure 4. At all cones, the addition of grog decreases the burning shrinkage. It is of importance to note that the grog decreases the tendency of the body to over-fire at cones 15 and 20.

Figure 5. Increasing the grog weakens the body up to the point where over-fire destroys the structure of the body made without grog.

Figure 6. In general, the addition of grog raises the apparent specific gravity. Above 25 percent grog, the increase is small.

Figure 7. With each addition of grog, the apparent porosity is markedly increased. Here again it is shown that objectionable over-fire can be greatly diminished by addition of grog.

Series B.—Effect of Size of Grog.

Figure 8. The amount of water required to develop plasticity increases with the fineness of the grog used.

Figure 9. The linear drying shrinkage also increases with the fineness of grog used.

Figure 10. In general, the strength of the raw body increases as the fineness of the grog is increased. In this work, the 200-mesh grog gave a slightly reduced strength.

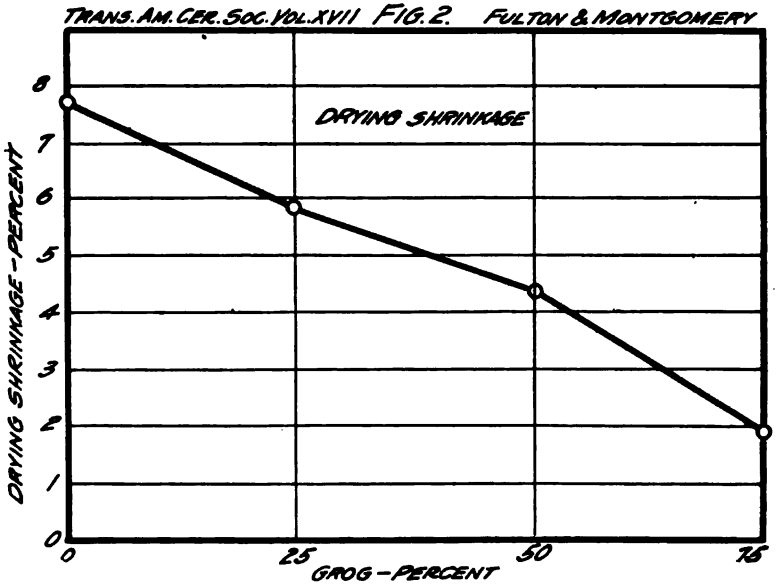

TRANS. AM. CER. SOC. VOL. XVII FIG. 2. FULTON & MONTGOMERY
DRYING SHRINKAGE
DRYING SHRINKAGE - PERCENT
0
1
2
3
4
5
6
7
8
0
25
50
75
GROG - PERCENT

FIG. 3.

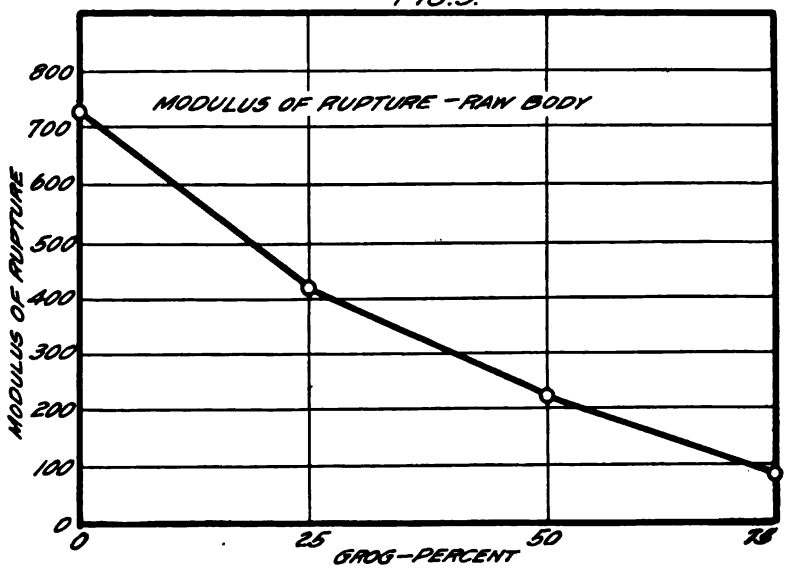

MODULUS OF RUPTURE - RAW BODY
MODULUS OF RUPTURE
0
100
200
300
400
500
600
700
800
0
25
50
75
GROG - PERCENT

Figure 11. With increased fineness of grog, the burning shrinkage is increased. This is most noticeable at cones 15 and 20. At cone 20, the bodies with 100 and 200-mesh grog show a decreased shrinkage due to over-firing.

Figure 12. Up to cone 15, increased fineness of the grog increases the strength of the body as shown by the modulus of rupture curves. At cone 20, the effect of over-firing is very evident. The modulus of rupture test shows this point more clearly than any other test, as the bodies with 14 and 35 mesh grog are here shown to be affected by over-firing.

Figure 13. The apparent specific gravity is little affected by the size of grog except at cone 20. Here, the increases in grog fineness causes a decrease in apparent specific gravity until the grog becomes finer than 35 mesh, when there is an increase in apparent specific gravity with 100 and 200 mesh grog.

Figure 14. At cone 010 and cone 5, the apparent porosity increases with the fineness of grog, while at cone 10 there is little or no effect. When burned to cones 15 and 20, the apparent porosity is decreased with increase in grog fineness except at cone 20, where the over-fire affects the bodies with 100 and 200 mesh grog.

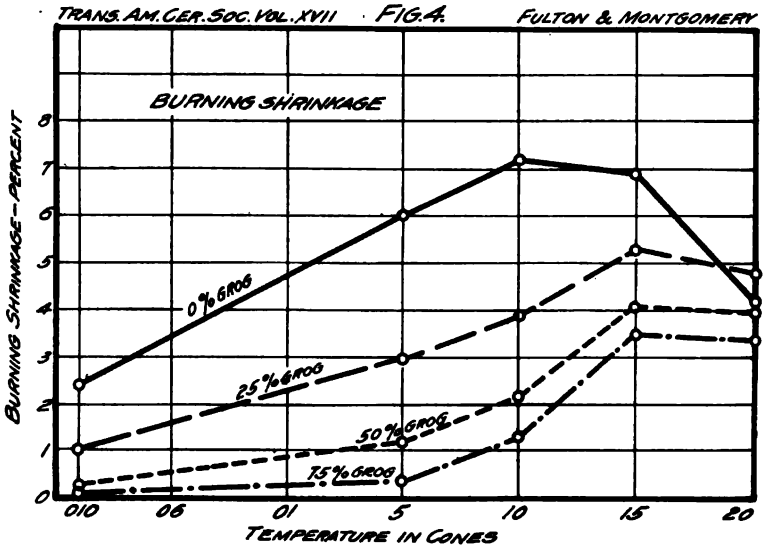
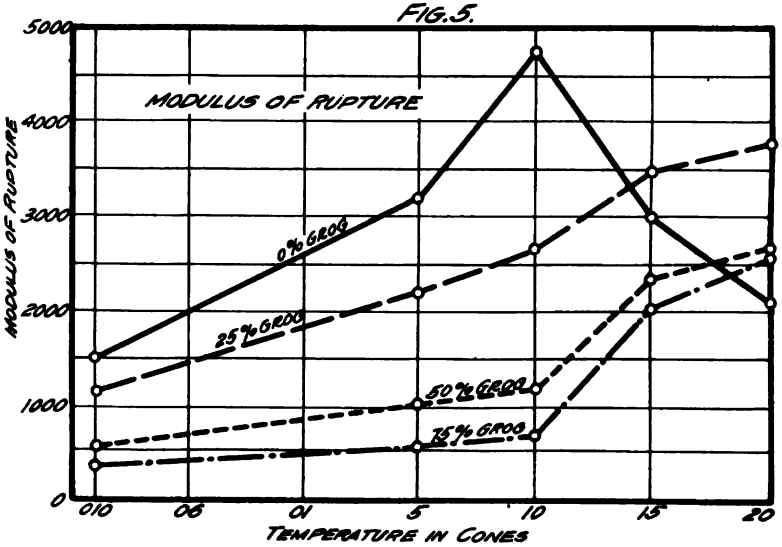
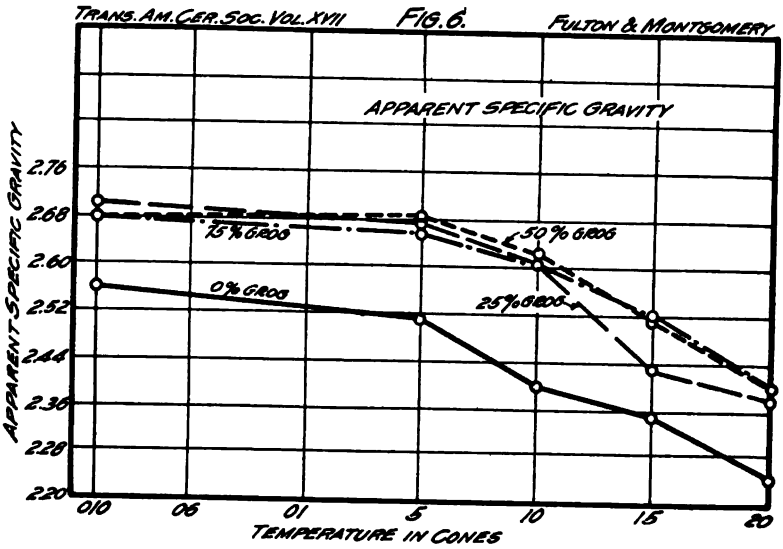

TRANS. AM. CER. SOC. VOL. XVII
FIG. 4.
FULTON & MONTGOMERY
BURNING SHRINKAGE
BURNING SHRINKAGE - PERCENT
0% GROG
25% GROG
50% GROG
75% GROG
0
1
2
3
4
5
6
7
8
010
06
01
5
10
15
20
TEMPERATURE IN CONES

FIG. 5.


MODULUS OF RUPTURE
MODULUS OF RUPTURE
0% GROG
25% GROG
50% GROG
75% GROG
0
1000
2000
3000
4000
5000
010
06
01
5
10
15
20
TEMPERATURE IN CONES


TRANS. AM. CER. SOC. VOL. XVII
FIG. 6.
FULTON & MONTGOMERY
APPARENT SPECIFIC GRAVITY
APPARENT SPECIFIC GRAVITY
2.76
2.68
2.60
2.52
2.44
2.36
2.28
2.20
75% GROG
50% GROG
0% GROG
25% GROG
010
06
01
5
10
15
20
TEMPERATURE IN CONES

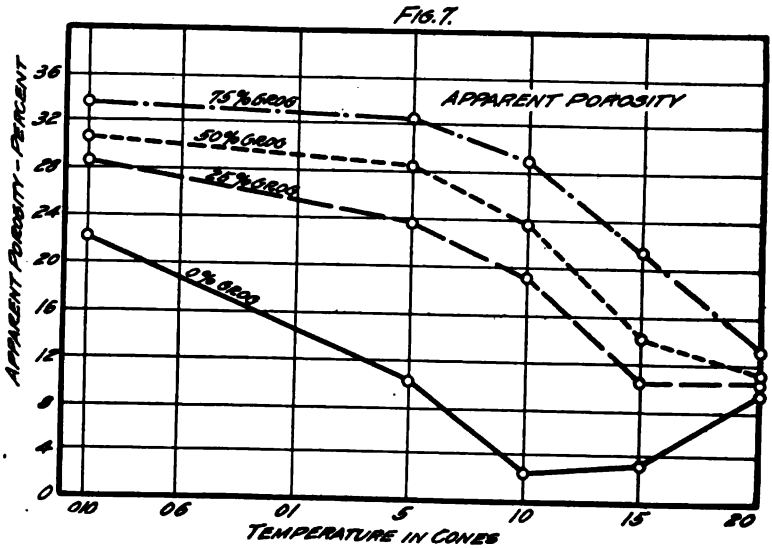


FIG. 7.
APPARENT POROSITY
APPARENT POROSITY - PERCENT
36
32
28
24
20
16
12
8
4
0
75% GROG
50% GROG
25% GROG
0% GROG
010
06
01
5
10
15
20
TEMPERATURE IN CONES

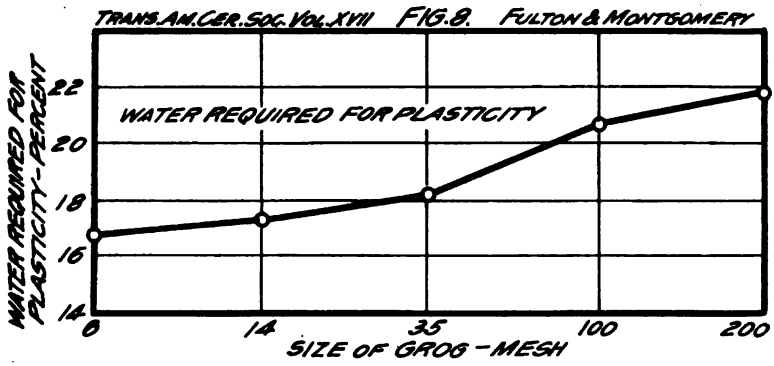

TRANS. AM. CER. SOC. VOL. XVII FIG. 8. FULTON & MONTGOMERY
WATER REQUIRED FOR PLASTICITY
WATER REQUIRED FOR PLASTICITY - PERCENT
22
20
18
16
14
0
14
35
100
200
SIZE OF GROG - MESH

FIG. 9.

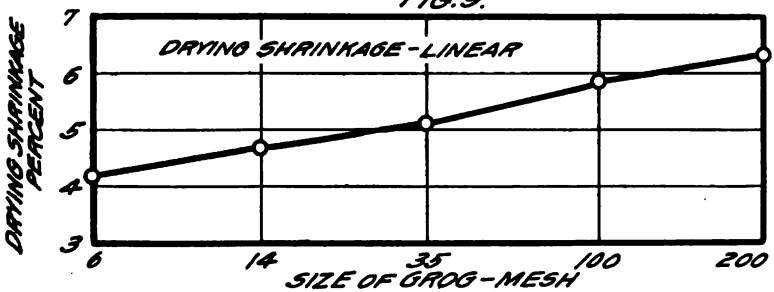
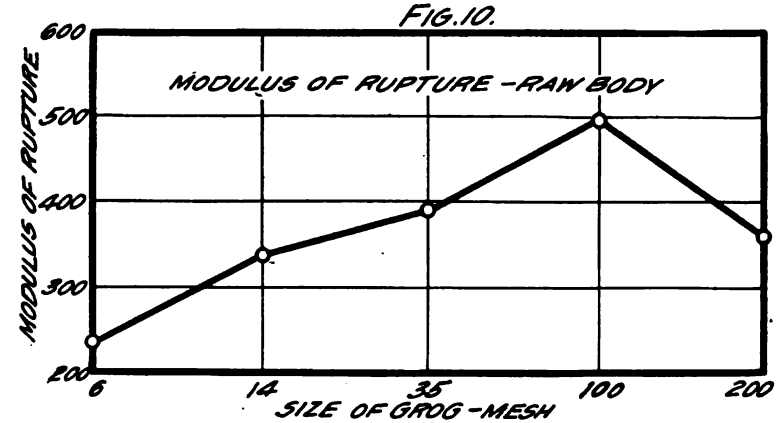

DRYING SHRINKAGE - LINEAR
DRYING SHRINKAGE PERCENT
7
6
5
4
3
6
14
35
100
200
SIZE OF GROG - MESH

FIG. 10.


MODULUS OF RUPTURE - RAW BODY
MODULUS OF RUPTURE
600
500
400
300
200
6
14
35
100
200
SIZE OF GROG - MESH

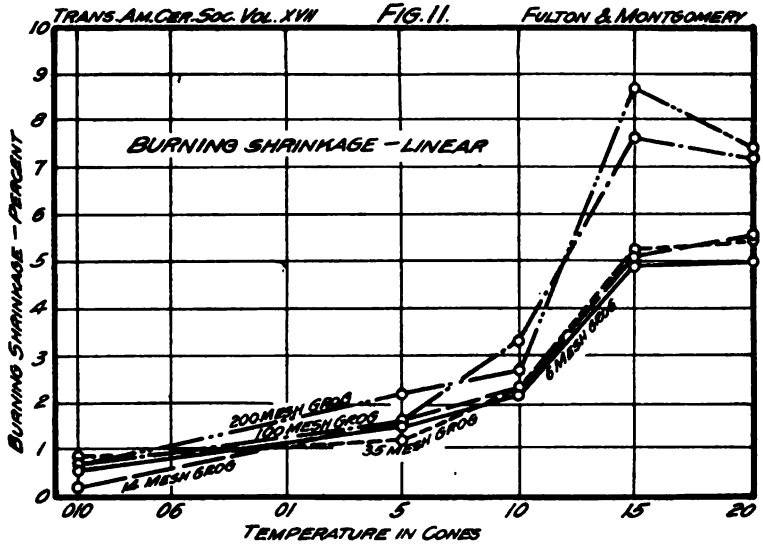
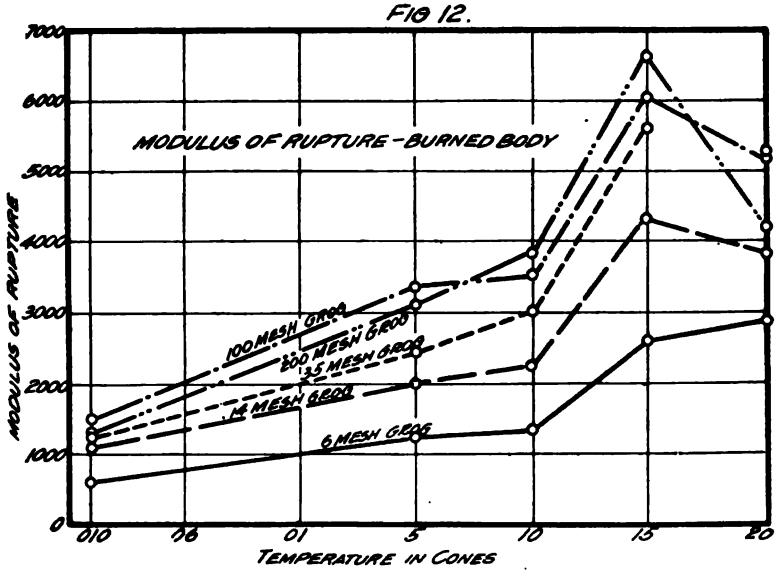

TRANS. AM. CER. SOC. VOL. XVII
FIG. 11.
FULTON & MONTGOMERY
BURNING SHRINKAGE - LINEAR
BURNING SHRINKAGE - PERCENT
200 MESH GROG
100 MESH GROG
35 MESH GROG
14 MESH GROG
6 MESH GROG
010
06
01
5
10
15
20
TEMPERATURE IN CONES

FIG 12.


MODULUS OF RUPTURE - BURNED BODY
MODULUS OF RUPTURE
100 MESH GROG
200 MESH GROG
35 MESH GROG
14 MESH GROG
6 MESH GROG
010
06
01
5
10
15
20
TEMPERATURE IN CONES

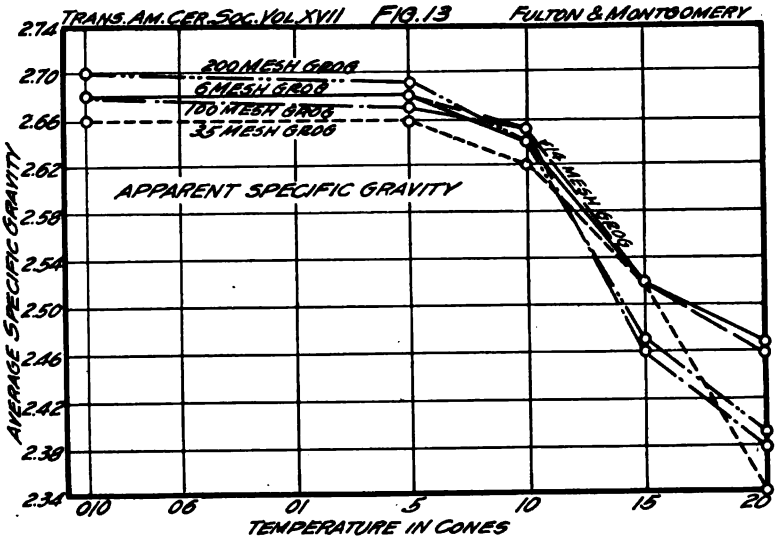
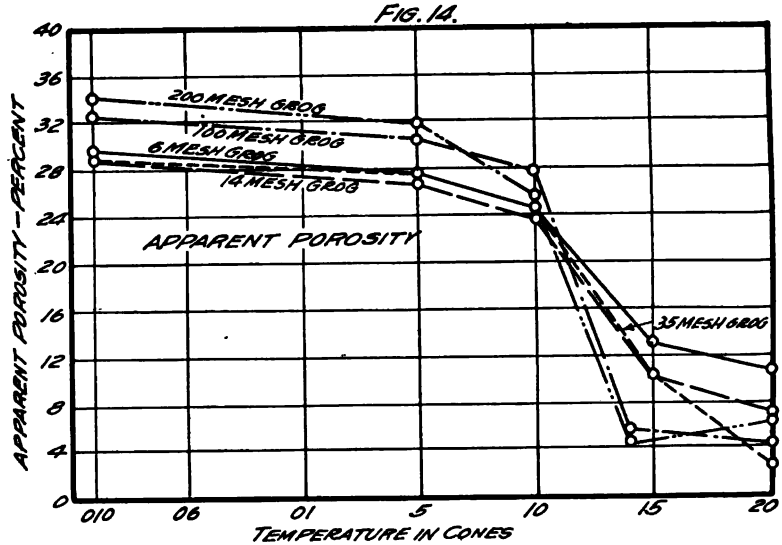

TRANS. AM. CER. SOC. VOL. XVII FIG. 13 FULTON & MONTGOMERY
200 MESH GROG
6 MESH GROG
100 MESH GROG
35 MESH GROG
14 MESH GROG
APPARENT SPECIFIC GRAVITY
AVERAGE SPECIFIC GRAVITY
2.74
2.70
2.66
2.62
2.58
2.54
2.50
2.46
2.42
2.38
2.34
010
06
01
5
10
15
20
TEMPERATURE IN CONES

FIG. 14.


200 MESH GROG
100 MESH GROG
6 MESH GROG
14 MESH GROG
35 MESH GROG
APPARENT POROSITY
APPARENT POROSITY — PERCENT
40
36
32
28
24
20
16
12
8
4
0
010
06
01
5
10
15
20
TEMPERATURE IN CONES

THE ELECTRICAL CONDUCTIVITY OF A PORCELAIN MIXTURE AND A SHALE UPON HEATING[1]

BY CHAS. S. KINNISON, PITTSBURGH, PA.

It was at one time supposed that silicate melts and volcanic magmas were of the nature of alloys. Barus and Iddings[2] were perhaps among the first to show that they possessed electrical conductivity. In their researches they used silicates having an SiO_2 content ranging from 48.5 percent to 75.5 percent, and showed that the materials had a very large positive temperature coefficient. Doelter has shown that basalt can be electrolyzed, as was proven by an accumulation of iron at the cathode. These facts show that silicates are not similar to alloys, but rather that they behave as electrolytes and represent dissociated solutions.

The work described in this paper consists of a study along these lines, using a typical porcelain mixture and Bedford shale as the silicates. For making such a study, each of these materials was fashioned into a small cylinder $\frac{9}{16}$ inch in diameter and $\frac{3}{4}$ inch long. In each end of the cylinder and at a distance of $\frac{1}{2}$ inch apart, the electrodes were imbedded. These consisted of circular platinum discs $\frac{3}{8}$ inch in diameter, to which were attached platinum wires four inches in length. The latter served the purpose of conductors and held the specimens in the electric furnace, which was of the platinum wound resistance type. The rate of temperature increase was kept as near as possible to 10° per ten minutes. Each material was carried to an ultimate temperature sufficient to bring about vitrification, this being 1400°C. in the case of the porcelain and 1150°C. for the shale.

During the progress of the heating, measurements of the electrical conductivity were made by means of a Leeds and Northrup testing set, type S, whose principle of operation is that of the Wheatstone bridge. An alternating current and a telephone attachment were used for obtaining a balance of the

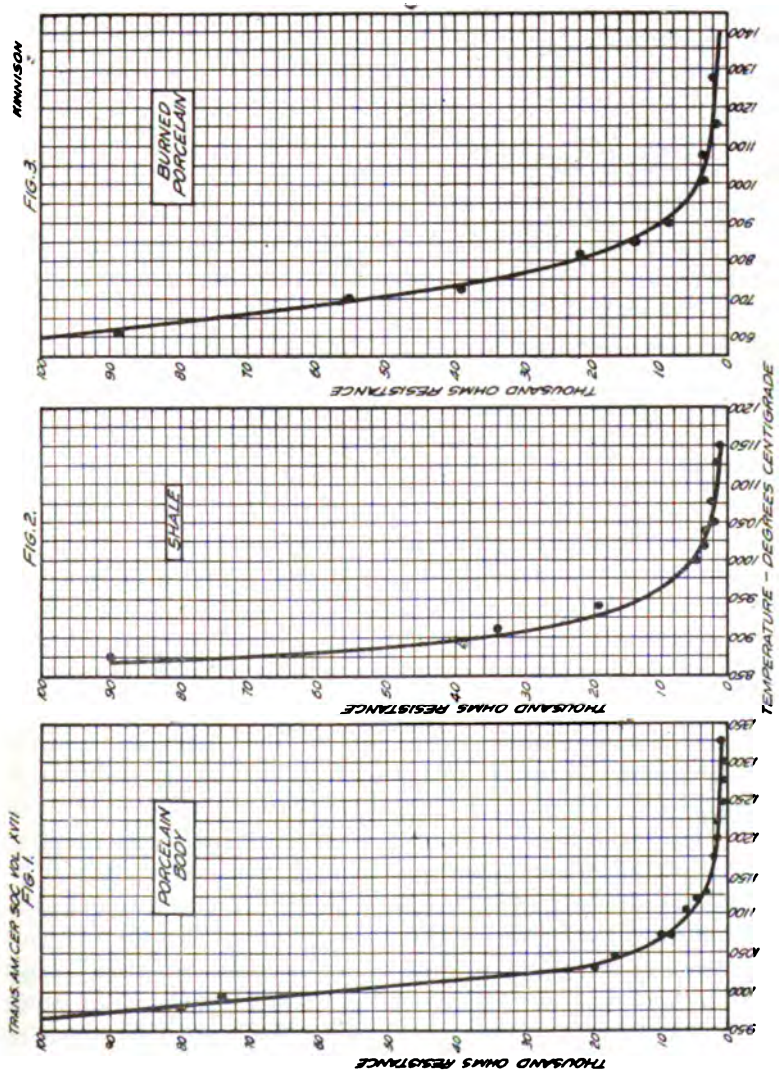
[1] By permission of the Director, Bureau of Standards.
[2] *Amer. Jour. Sc.*, 44, 242, 1892.

circuit. As soon as the resistance dropped to a point where it could be fairly accurately measured observations were begun, and readings were made at intervals of about every 20°. The results are compiled in Tables I, II and III and are shown graphically in Figs. 1, 2 and 3.

There are several sources of error in making these measurements, among them being the formation of bleb structure caused by the evolution of gases which causes discontinuity in the structure of the mass and therefore increases the resistance; another source is the uncertainty of knowing when the specimen has reached thermal equilibrium, or, in other words, when the temperature of the specimen is that of the furnace. It is thought that the rate used was slow enough to enable equilbrium to be reached. Another error is that due to the shortening of the specimen during firing which caused the length of the cylindrical section to decrease and hence the resistance during the early and later parts of the run are not in the ratio of the specific resistances.

Two methods of electrical conduction are to be recognized, viz., metallic or electron conduction, and ionic or electrolytic conduction. The current is carried in a copper wire, for instance, by the former method, and by the latter method in the case of salt solutions or any other solution containing ions. In the case of silicates, such as we have here, we probably have examples of both. At the lower temperatures where the material still exists as a powder, we may assume that the conduction is due to electrons. The location of the true minimum tone point is difficult to determine and the resistance is very high. The accuracy of the values found at low temperatures is therefore doubtful. When the material experiences incipient vitrification or sintering, conduction is due partially to some ionization. Finally when the softening point of the principal composite eutectic is reached, conduction is due mostly, perhaps, to the ions.

The general shape of the curves shown will be observed to be quite similar. They consist, generally speaking, of two portions, one part being a steep straight line and the other a some-


ANNISON
FIG. 3.
BURNED PORCELAIN
THOUSAND OHMS RESISTANCE
FIG. 2.
SHALE
THOUSAND OHMS RESISTANCE
TEMPERATURE - DEGREES CENTIGRADE
TRANS. AM. CER. SOC. VOL. XVIII
FIG. 1.
PORCELAIN BODY
THOUSAND OHMS RESISTANCE

what flat or horizontal line. The former shows the conductivity of the solid and the latter that of the fused or liquid material. It is to be observed also that the steep portion of the curve represents a very high temperature coefficient, while the flatter part represents one correspondingly small. The significance of this, of course, is that a difference of 10°, for instance, in the temperature makes a decided variation in the conductivity of the material while it is in the solid state, and but a relatively slight change when the material has become fused.

The intersection of these two parts of the curve indicates the transition point from the solid to the liquid phase, the degree of sharpness or distinctness of this point varying with the abruptness of the melting point. If the softening point be sharp and clearly discernible, then the intersection will be more or less distinct. If, on the other hand, the softening takes place slowly, as is the case with the materials used, the intersection of the two portions of the curve will be gradual, as the figures show.

We are familiar with the softening behavior of a porcelain body and know also that Bedford shale has a good vitrification range. These facts are confirmed by the curves. In fact, this might be a method of establishing the relative length of the vitrification ranges of different clays. It is to be expected that, in calcareous clays, or silicates, the intersection point mentioned above could be clearly recognized.

After the porcelain specimen had been used in the above work and was therefore porcelain in structure, its conductivity in that state was studied. Figure 3 shows the relation between the temperature and resistance. The general shape of the curve in Fig. 3 is that of the curves in Figs. 1 and 2. It will be noticed, however, that its temperature coefficient is much smaller before the material softens than in the other two curves. This is to be expected, because there is not so much chemical change in progress and there is therefore, less ionization. In other words, a given change in temperature does not bring about as large a change in the resistance, because it does not bring about so marked a change in the degree of dissociation. The gradual increase in conductivity is explained by the gradual lowering of

the viscosity, allowing greater freedom for the migration of the ions.

Rasch and Hinrichsen[2] using the well known van't Hoff formula,

$$\frac{drlu}{dT} = \frac{-q}{WT^2}$$

have deduced the equation $\frac{dr}{r} = -\frac{V'dT}{T^2}$, where r = the conductivity, T the absolute temperature, and V' a constant. Integrating the above we have,

$$Log\ R = \frac{v}{T} + C$$

where R is the specific resistance, and v and C are constants dependent on the material. We are able, therefore, to show the temperature resistance relation graphically by plotting the logarithm of the resistance as the ordinate and $\frac{1}{T}$ as the abscissa.

Figures 4, 5 and 6 have been plotted in this manner and show a few points that are not apparent from the other curves. In Figure 4 we have two rather marked changes in the trend of the curve. At about 980-1000° there is to be noticed the first change. This probably represents the temperature at which sintering begins, brought about by the small amount of fluxes introduced through the ball clay. At 1125-1135° a more marked change is noticeable and probably represents the point at which the feldspar begins its action. From here on the curve is fairly smooth indicating gradual softening.

In Figure 5, representing the shale, we have two somewhat similar points. The first one at 875° probably represents the melting point of the most fusible eutectic mixture, while that at about 1080-1100° is the softening point of the principal eutectic. Figure 6, representing the burned porcelain specimen, shows an absence of such irregularities until its softening point is approached. The absence of irregularities in this curve tends to

[2] *Zeit. fur Elektroch*, 14, 41, 1908.

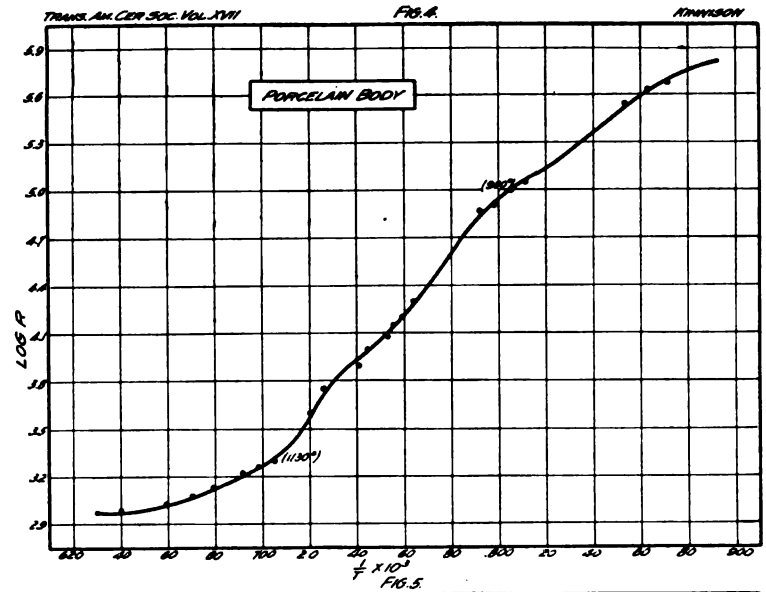
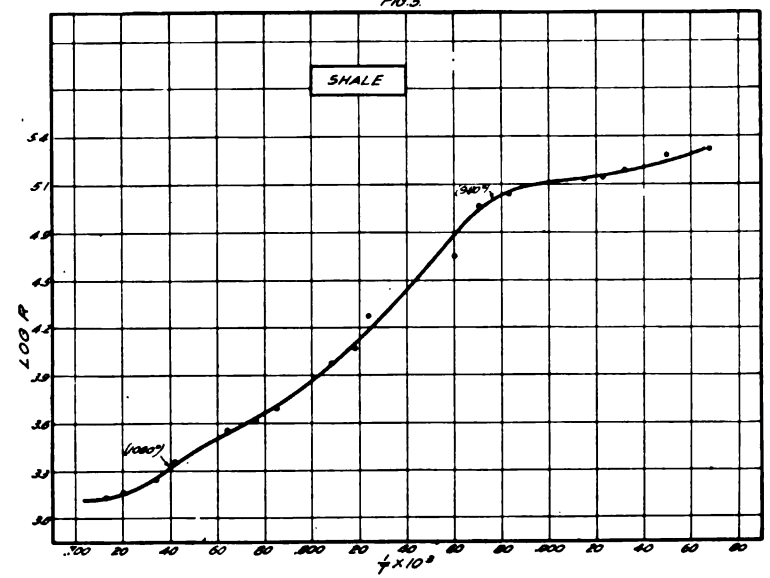
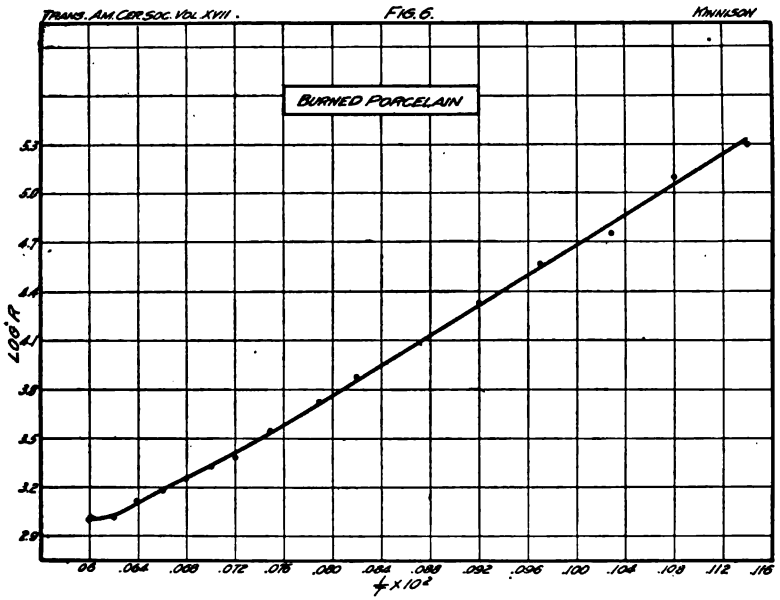

TRANS. AM. CER. SOC. VOL. XVII
FIG. 4.
ATKINSON
PORCELAIN BODY
(1130°)
LOG ρ
1/T X 10⁴

FIG. 5.


SHALE
(1080°)
(940°)
LOG ρ
1/T X 10⁴

show that there are practically no chemical changes until the softening point is reached, as we might reasonably expect.

The results of the foregoing work tend to show that these silicates do not conduct like alloys, but rather that they behave as electrolytes and show dissociation. A molten condition of the material is not prerequisite to the presence of ions, since polarization phenomena have been observed at temperatures several hundred degrees below the melting point. The large differences in the conductivity are due not so much to a change in the con-



centration of the ion as the speed with which they are permitted to travel, this being controlled almost entirely by the viscosity.

Mr. A. V. Bleininger has suggested that the softening point of the principal composite eutectic of a clay can be established by determining the electrical resistance and plotting the results as the log of R and the reciprocal of the absolute temperature. Thus, this point is represented as being at about 1130°C. in the case of the porcelain body and at about 1090° in the case of the shale.

Acknowledgment and thanks are herewith tendered Mr. Bleininger for suggesting the subject of the foregoing work and for his assistance. Free reference has been made also to C. Doelter's work appearing in the Handbuch der Mineralchemie, Vol. I, part 5.

TABLE I—PORCELAIN BODY

TEMPERATURE DEGREES CENTIGRADE	TEMPERATURE ABSOLUTE	OHMS R	$\frac{1}{T}$	LOG R
860	1133	650000	$.882 \times 10^{-3}$	5.813
875	1148	500000	$.871 \times 10^{-3}$	5.699
885	1158	440000	$.864 \times 10^{-3}$	5.643
900	1173	400000	$.853 \times 10^{-3}$	5.602
960	1233	110000	$.811 \times 10^{-3}$	5.041
970	1243	100000	$.805 \times 10^{-3}$	5.000
980	1253	80000	$.798 \times 10^{-3}$	4.903
990	1263	74000	$.792 \times 10^{-3}$	4.869
1035	1308	20000	$.764 \times 10^{-3}$	4.301
1045	1318	16000	$.759 \times 10^{-3}$	4.204
1050	1323	14000	$.756 \times 10^{-3}$	4.146
1055	1328	12000	$.753 \times 10^{-3}$	4.079
1070	1343	10000	$.745 \times 10^{-3}$	4.000
1075	1348	8000	$.742 \times 10^{-3}$	3.903
1105	1378	5600	$.726 \times 10^{-3}$	3.748
1115	1388	4000	$.720 \times 10^{-3}$	3.602
1125	1398	2800	$.715 \times 10^{-3}$	3.447
1135	1408	2350	$.710 \times 10^{-3}$	3.371
1145	1418	2000	$.705 \times 10^{-3}$	3.301
1160	1433	1800	$.698 \times 10^{-3}$	3.255
1175	1448	1650	$.691 \times 10^{-3}$	3.217
1200	1473	1350	$.679 \times 10^{-3}$	3.130
1220	1493	1200	$.670 \times 10^{-3}$	3.079
1245	1518	1050	$.659 \times 10^{-3}$	3.021
1275	1548	950	$.646 \times 10^{-3}$	2.978
1290	1563	920	$.640 \times 10^{-3}$	2.964
1315	1588	950	$.630 \times 10^{-3}$	2.978

TABLE II—SHALE

TEMPERATURE DEGREES CENTIGRADE	TEMPERATURE ABSOLUTE	OHMS R	$\frac{1}{T}$	LOG R
755	1028	230000	$.973 \times 10^{-3}$	5.362
760	1033	210000	$.968 \times 10^{-3}$	5.322
780	1053	200000	$.950 \times 10^{-3}$	5.301
800	1073	155000	$.932 \times 10^{-3}$	5.190
810	1083	140000	$.923 \times 10^{-3}$	5.146
820	1093	135000	$.915 \times 10^{-3}$	5.130
840	1113	132000	$.898 \times 10^{-3}$	5.120
860	1133	110000	$.883 \times 10^{-3}$	5.041
875	1148	90000	$.871 \times 10^{-3}$	4.954
890	1163	45000	$.860 \times 10^{-3}$	4.653
910	1183	33000	$.845 \times 10^{-3}$	4.519
940	1213	19000	$.824 \times 10^{-3}$	4.278
950	1223	12000	$.818 \times 10^{-3}$	4.079
965	1248	9500	$.808 \times 10^{-3}$	3.978
1000	1273	5000	$.785 \times 10^{-3}$	3.669
1015	1288	4200	$.776 \times 10^{-3}$	3.623
1035	1308	3600	$.764 \times 10^{-3}$	3.556
1050	1323	3000	$.756 \times 10^{-3}$	3.477
1065	1338	2500	$.748 \times 10^{-3}$	3.398
1075	1348	2300	$.742 \times 10^{-3}$	3.362
1080	1353	2100	$.739 \times 10^{-3}$	3.322
1095	1368	1750	$.734 \times 10^{-3}$	3.243
1115	1388	1460	$.720 \times 10^{-3}$	3.164
1130	1403	1340	$.713 \times 10^{-3}$	3.127
1150	1423	1300	$.703 \times 10^{-3}$	3.114

TABLE III—BURNED PORCELAIN

TEMPERATURE DEGREES CENTIGRADE	TEMPERATURE ABSOLUTE	OHMS R	$\frac{1}{T}$	LOG R
600	873	200000	$.114 \times 10^{-2}$	5.301
650	923	130000	$.108 \times 10^{-2}$	5.114
695	968	55000	$.103 \times 10^{-2}$	4.740
760	1033	37000	$.097 \times 10^{-2}$	4.568
810	1083	22000	$.092 \times 10^{-2}$	4.342
860	1133	14100	$.088 \times 10^{-2}$	4.149
900	1173	9900	$.085 \times 10^{-2}$	3.995
950	1223	7230	$.082 \times 10^{-2}$	3.859
990	1263	5400	$.079 \times 10^{-2}$	3.732
1035	1308	4000	$.076 \times 10^{-2}$	3.602
1075	1348	3100	$.074 \times 10^{-2}$	3.491
1115	1388	2520	$.072 \times 10^{-2}$	3.401
1155	1428	2120	$.070 \times 10^{-2}$	3.326
1200	1473	1780	$.068 \times 10^{-2}$	3.250
1235	1508	1520	$.066 \times 10^{-2}$	3.182
1295	1548	1320	$.064 \times 10^{-2}$	3.120
1315	1588	1150	$.063 \times 10^{-2}$	3.060
1350	1623	1040	$.062 \times 10^{-2}$	3.017
1400	1673	920	$.060 \times 10^{-2}$	2.964

RESULTS OF COMPRESSION TESTS ON PORCELAIN BASE

BY J. W. WARD

The object is to provide an insulated base for the support and insulation of electric conductors, and especially for currents of high voltage, and the data given is the result of tests obtained on a design consisting of a series of plates and discs built in combination and constructed of solid material.

The total height was limited to 10½ inches and the diameter to 14 inches, including petticoats or corrugations, the top and bottom being provided with metal castings. The actual porcelain area for supporting load was 8⅞ inches in diameter by 9 inches high.

The porcelain body used in the construction of test pieces was from a standard commercial porcelain insulator body, the thickness of each disc not being over 1¼ inch in any case. The test specimens were made by the plastic jigger method, fired in an up-draft kiln to cone 10. The green ware or test pieces were dried slowly for fourteen days before being placed in the kiln.

The porcelain discs were assembled together and held in place by portland cement, the cement being mixed and used in accordance with standard specifications approved by the American Society of Testing Materials.

The assembled porcelain for one test piece, without metal cap or base, weighed 85 pounds, and with the metal parts assembled the total weighed 120 pounds.

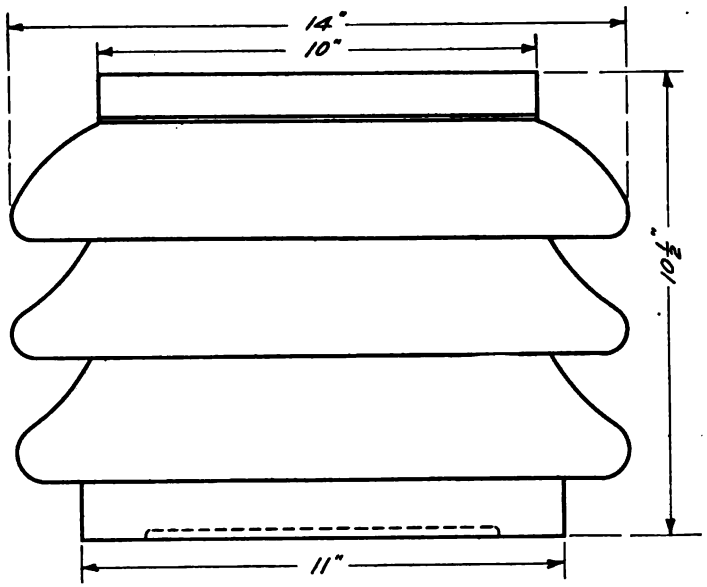
Figure 1 shows an elevation of test piece assembled. Figure 2 shows the finished test piece after being subjected to a 600,000 pound compression load. All outside surfaces, or those which would be subjected to the weather, were glazed a mahogany or brown glaze.

Tests were made on one lot of six samples on an Olsen 600,000 pound testing machine having one fixed, and one spherical bearing plate. The first lot of samples tested broke down on

mechanical test from 350,000 to 500,000 pounds on account of the method used in assembling sections together. Examination showed that large areas from 2 inches to 3 inches in diameter were not properly cemented together, and that from 25 to 35 percent of the area was not made use of.

The second test covering a lot of six pieces was made on an Olsen testing machine and none of the samples failed after being tested to the 600,000 pounds capacity of the machine. The third

TRANS. AM. CER. SOC. VOL. XVII FIG. 1. WARD



lot of six test pieces were tested on an Emery precision testing machine having a capacity in compression of 2,300,000 pounds. The machine is of the horizontal type and consists of a straining press mounted on wheels and a weighing end mounted on a bed, with the press and weighing ends connected by two screws. The press is double acting, driven by hydraulic accumulators, and the load transmitted to the specimen from the press is carried through the specimen to the hydraulic supports and the weighing end of the machine.

The tabulated list shown in the table gives the results of tests on the third lot. The readings represented by the numbers in the first column were taken from the first crackling noise that could be detected while the test was progressing. The first click or indication of load, ranged from six to eight minutes after test was applied, the final time for complete failure being as follows:

Test No. 1—Complete failure—11 minutes
Test No. 2—Complete failure—12 minutes
Test No. 3—Complete failure—12 minutes
Test No. 4—Complete failure—13 minutes
Test No. 5—Complete failure—10 minutes
Test No. 6—Complete failure—13 minutes

An examination of the test specimens under test did not reveal any cracks on the outside surface up to 400,000 pounds. At 500,000 pounds fine hair-like cracks were noticed on the outside diameters through the surface of the glaze. At 650,000 pounds small pieces of the test specimens began to fall from the outside diameters, and this continued until end of test, reducing the diameter until the final break, when there would be a small explosion, and the test piece would fly to pieces.

Some of the test pieces showed small breaks or air spaces in the cement joints, and the presence of these will help account for some of the variation in results obtained. A close examination of several hundred pieces of the broken test pieces showed thoroughly vitrified porcelain free from cracks, blebs, fish tails, etc.

The total pressure area was equal to 62 square inches, and the average pressure in pounds per square inch at breaking point for the last six tested is as follows:

Test No. 1—1 118.000=18,100 pounds per square inch
Test No. 2—1,116.000=18,050 pounds per square inch
Test No. 3—1,072,000=17,650 pounds per square inch
Test No. 4—1,052,000=17,100 pounds per square inch
Test No. 5—1,156,000=18,700 pounds per square inch
Test No. 6—1,098,000=17,750 pounds per square inch
Average breaking load=1,102,000 pounds
Average breaking load per square inch=17,890 pounds

A summary of results shows that it is possible to get high crushing strength in a commercial porcelain body, but it is essential in assembling the several elements together that there be no breaks or air spaces in the joints, if the maximum strength is to be obtained. Neat portland cement will, if used properly,

FIG. 2

fill up any irregularities due to distortion in drying or firing operations. Had conditions allowed, we could have used sheets of lead to fill up the depressions, and with a material as a filler at the joints, that would flow slightly, additional strength could have been added to the ultimate breaking point.

TABLE I

NO.	TEST No. 1	TEST No. 2	TEST No. 3	TEST No. 4	TEST No. 5	TEST No. 6
1	376.000	265.000	263.000	278.000	306.000	269.000
2	458.000	370.000	325.000	300.000	344.000	315.000
3	510.000	404.000	416.000	345.000	429.000	405.000
4	520.000	444.000	452.000	388.000	468.000	486.000
5	538.000	476.000	457.000	430.000	515.000	526.000
6	663.000	486.000	467.000	455.000	530.000	629.000
7	715.000	510.000	500.000	475.000	562.000	666.000
8	730.000	530.000	527.000	495.000	580.000	691.000
9	770.000	568.000	580.000	588.000	610.000	729.000
10	810.000	619.000	590.000	606.000	662.000	785.000
11	842.000	730.000	653.000	630.000	700.000	807.000
12	861.000	793.000	661.000	686.000	835.000	815.000
13	1,118.000	862.000	750.000	749.000	945.000	880.000
14	.....	910.000	856.000	753.000	985.000	910.000
15	.....	928.000	868.000	783.000	1,030.000	923.000
16	.....	970.000	884.000	849.000	1,156.000	934.000
17	.....	1,005.000	905.000	886.000	.....	964.000
18	.....	1,095.000	935.000	894.000	.....	996.000
19	.....	1,116.000	955.000	987.000	.....	1,019.000
20	.....	.....	1,072.000	1,014.000	.....	1,098.000
21	.....	.....	.....	1,052.000	.....	.....

INFLUENCE OF VARYING WATER CONTENT IN A FIRE CLAY MIXTURE

BY R. J. MONTGOMERY AND C. E. FULTON

Whenever a clay or a mixture of clays is made into a plastic working mass, the question of influence of the water content must necessarily have consideration. Just what influence the percent of water used has on the physical structure of the clay during the drying and burning periods is not fully understood, although it has been the general impression that the structure of the finished ware is affected to a greater or less extent.

In the manufacture of many products, it is customary for the individual workman to desire a certain consistency of the clay. This consistency varies considerably with different workmen. In other cases when the clay is handled by machine only and not by hand, the water content may vary quite widely through carelessness of workmen or lack of consideration of the subject.

The present paper gives some data on experimental work carried on in our laboratory to show how large the variation in water content may be, without materially affecting the physical structure during drying and burning.

The data herein submitted are the results of tests on two samples.

1. St. Louis fire clay.
2. A mixture of 50 percent St. Louis fire clay and 50 percent of the same material burned to about cone 6.

The raw clay was ground to pass through 20 mesh and the burnt clay to pass through a 10 mesh screen, Tyler Standard Scale Screen.

Tests Made. Both the clay and the clay-grog mixture were mixed with four different percentages of water, care being taken to reach the two extremes. These extremes were well beyond the best working consistency, being as soft and as stiff as possible to still allow molding. Test bars 1.25 in. by .75 in. by 5 in. were

made and marked for drying shrinkage. After careful drying, the shrinkages were measured, and some of the bars were broken to obtain the modulus of rupture of the raw clay. The remaining bars were burned to various cone temperatures to determine the physical properties in the burned state.

TABLE I—ST. LOUIS FIRE CLAY

TEST	1	2	3	4
Plasticity water	19.1	21.5	24.5	27.0
Drying shrinkage	5.8	7.7	8.6	9.8
Modulus of rupture of raw clay	508	723	735	664
Burning shrinkage—				
cone 010	2.3	2.4	2.5	2.6
cone 5	6.3	6.0	5.9	5.9
cone 10	7.2	7.2	7.1	6.6
cone 15	6.3	6.9	6.6	6.9
cone 20	4.1	4.2	4.8	4.5
Modulus of rupture—				
cone 010	1775	1500	1158	1161
cone 5	2879	3193	3007	4185
cone 10	3641	4753	4511	4964
cone 15	3742	3033	3098	5022
cone 20	1765	2111	2062	3416
Apparent sp. gr.—				
cone 010	2.59	2.56	2.56	2.58
cone 5	2.52	2.51	2.50	2.50
cone 10	2.45	2.40	2.40	2.42
cone 15	2.37	2.35	2.37	2.36
cone 20	2.27	2.24	2.20	2.23
Apparent porosity—				
cone 010	22.3	22.3	22.1	22.9
cone 5	10.2	10.3	10.7	11.6
cone 10	4.1	2.3	2.7	3.8
cone 15	4.1	3.1	3.0	1.4
cone 20	9.6	9.4	7.1	4.5

Three burns were made at each temperature to insure correct results. The bars from each burn were tested separately, and the data tabulated are the averages of the three burns. Details of the testing methods are given in another contribution

from this laboratory published in this volume and entitled "Laboratory Methods for the Physical Testing of Fire Clays."

Table I gives the results of tests made on the sample of St. Louis fire clay, while Table II gives corresponding data for the mixture of 50 percent St. Louis fire clay and 50 percent burnt St. Louis fire clay.

TABLE II — 50 PERCENT ST. LOUIS FIRE CLAY, 50 PERCENT BURNT ST. LOUIS FIRE CLAY

TEST	1	2	3	4
Plasticity water	14.1	16.5	19.0	21.5
Drying shrinkage	3.3	4.4	4.9	5.9
Modulus of rupture of raw clay	196	220	189	181
Burning shrinkage—				
cone 010	0.5	0.2	0.3	0.1
cone 5	1.2	1.2	1.1	1.3
cone 10	2.3	2.2	1.6	2.3
cone 15	4.2	4.1	4.3	4.3
cone 20	4.0	4.0	4.4	3.9
Modulus of rupture—				
cone 010	579	538	546	451
cone 5	1023	1016	916	852
cone 10	1066	1208	1134	1030
cone 15	1899	2307	2155	2087
cone 20	2489	2678	2837	2437
Apparent sp. gr.—				
cone 010	2.68	2.68	2.68	2.68
cone 5	2.67	2.68	2.68	2.68
cone 10	2.62	2.62	2.65	2.61
cone 15	2.52	2.51	2.53	2.51
cone 20	2.40	2.40	2.45	2.39
Apparent porosity—				
cone 010	28.3	29.7	32.9	30.8
cone 5	26.3	28.4	29.2	29.1
cone 10	22.7	23.7	26.5	24.9
cone 15	13.1	14.1	16.4	15.9
cone 20	9.0	11.1	12.9	11.8

Curves. The appended curves show in graphic form the effect of the water content on the various properties of the two samples tested.

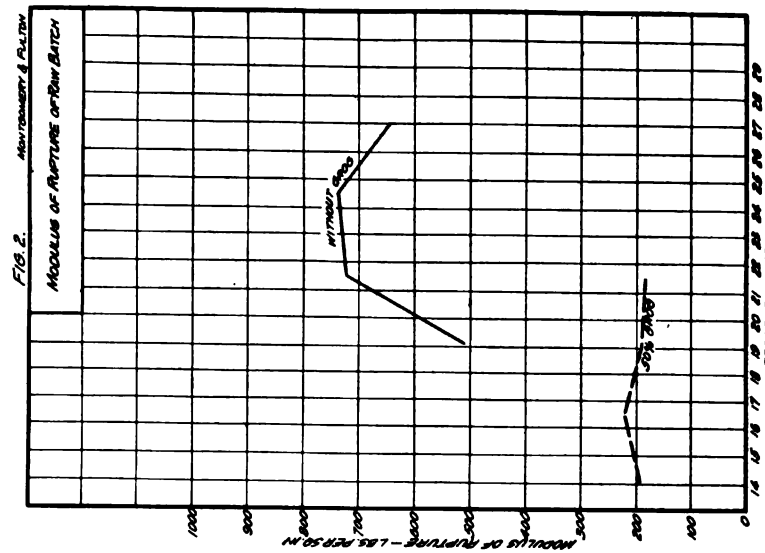
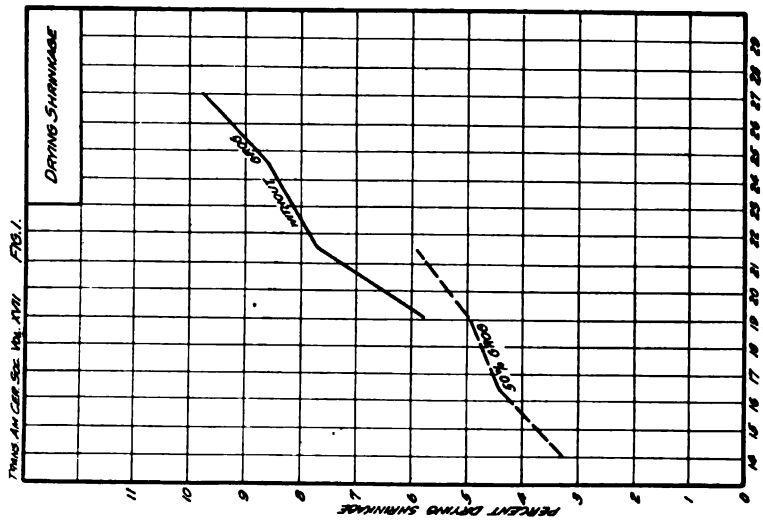


FIG. 2. MONTGOMERY & RUTH
MODULUS OF RUPTURE OF RAW BATCH
WITHOUT GROG
95% GROG
MODULUS OF RUPTURE — LBS. PER SQ. IN.
PERCENT WATER ADDED


TRANS AM CER. SOC. VOL. XVII FIG. 1.
DRYING SHRINKAGE
WITHOUT GROG
95% GROG
PERCENT DRYING SHRINKAGE
PERCENT WATER ADDED

A study of the tabulated data and the curves brings out the following points:

Figure 1. The drying shrinkage is greatly affected and is proportional to the amount of the water used.

Figure 2. The modulus of rupture shows an increase in strength with the first additions of water to the clay body, but it drops slightly, as the high extreme is reached. This is not noticed in the 50 percent grog body.

Figures 3 and 4. The burning shrinkage shows little or no effect of the water variations.

Figure 5. The higher percentages of water give a high strength at all cones, except cone 010 where the reverse is true. It will be noticed that between 21.5 percent and 24.5 percent water or within the normal working consistency there is little difference.

Figure 6. The 50 percent grog body does not show any marked variation with variation of water content.

Figure 7. The water content does not affect the apparent porosity until cone 15 is reached. At cones 15 and 20, the lowest percentage of water gives the greatest apparent porosity. Here again there is little difference between the two intermediate percentages.

Figure 8. In the 50 percent grog batch, the apparent porosity is affected at all cones, the lowest percentage of water giving the lowest apparent porosity. In a general way this is the reverse of the tendency shown in Figure 7.

Figures 9 and 10. The apparent specific gravity of both samples show little or no effect due to the variation in water content.

Conclusions. 1. The water content, if varied to any extent will affect the drying shrinkage and would have to be considered in factory practice where this is important.

2. The apparent porosity is affected to some extent, especially in the 50 percent grog mixture. The maximum variation is 4 percent, and within the normal working consistency this variation would be only 2½ to 3 percent. In most cases this would not be important.

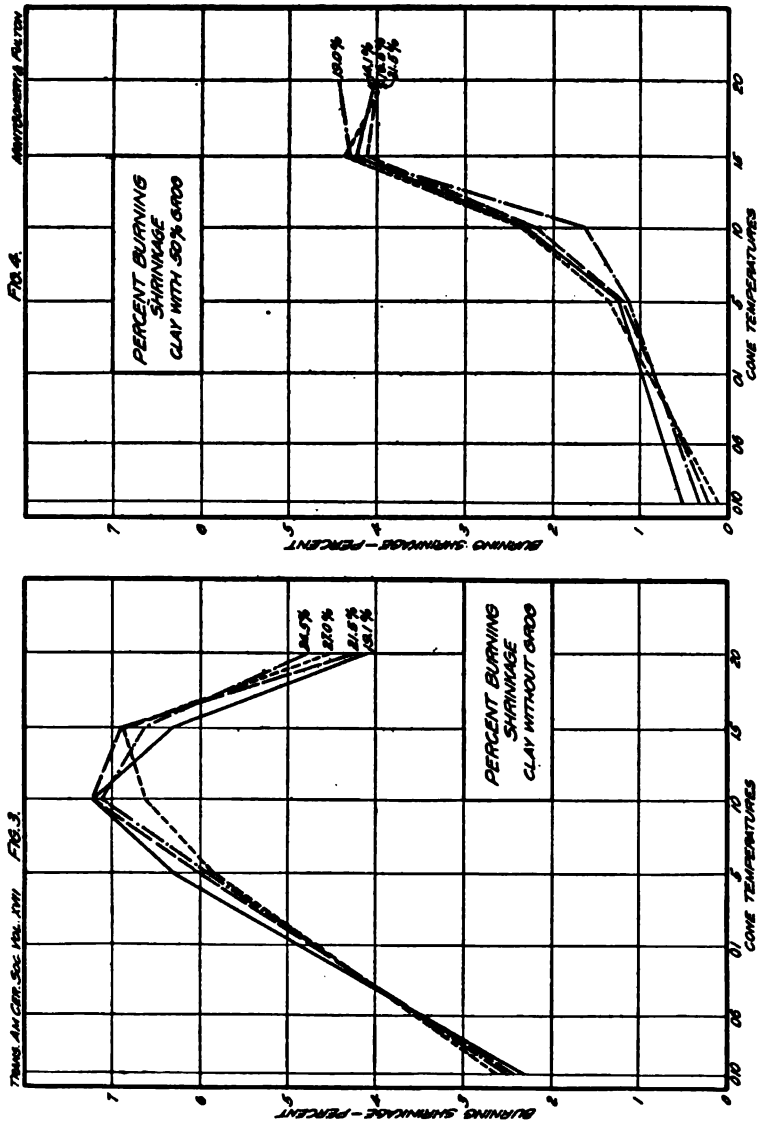


FIG. 4.
MONTGOMERY PATTEN
PERCENT BURNING SHRINKAGE CLAY WITH 50% GROG
BURNING SHRINKAGE - PERCENT
CONE TEMPERATURES
FIG. 3.
TRANS AM CER. SOC. VOL. XVII
PERCENT BURNING SHRINKAGE CLAY WITHOUT GROG
BURNING SHRINKAGE - PERCENT
CONE TEMPERATURES

3. In general, the data here presented show that for the samples tested any ordinary variation in water content will not change to any considerable extent the properties of the burned mass. The effect is greatest when the burning is carried to vitrification or beyond.

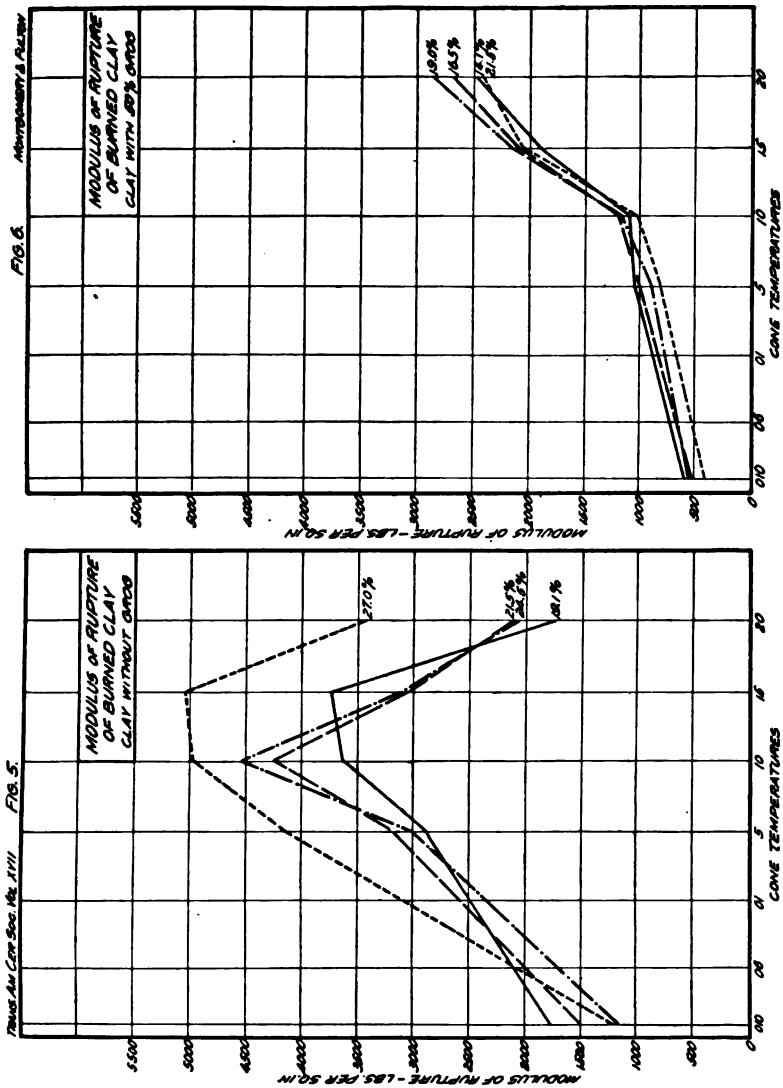
DISCUSSION

Mr. Purdy: May I ask how the modulus of rupture was obtained,—just what tests were used?

Mr. R. J. Montgomery: Small bars ½ by ¾ by 5 inches were burned to the cone temperatures noted in the body of the paper. These bars were broken in the standard modulus of rupture machine of the shot type.

Mr. Purdy: I think it is very important to emphasize that this laboratory is closely connected with one of the largest glass factories in the world, and they are constantly involved in the manufacture of pots and other fire clay parts necessary in the manufacture of plate glass, so this is not altogether theoretical. I don't know of a laboratory any closer allied to an actual work problem than they. I wish, however, to disagree with the statement that it matters not, what percentage of water is used in ordinary refractory wares. We find it makes a big difference just what water content you have. Take as in our case slabs, rings and saggers—the workability of the mass affects its ultimate strength when burned, and we must have the clay in just the right plastic condition to give us the maximum structural density or structural strength. It may not affect the modulus of rupture, but it will affect structure when you are having pieces joined, especially as in saggers where, as in a machine, you are forcing it up the side, or by hand you are welding the rings on to the bottom. We find it makes a difference whether you have a little or more water. The cause of this is altogether in the operator. Perhaps, I should have said for a given operator, the clay must be in a given condition of plasticity.

Mr. Yates: Every clay has a temper of its own, which is governed by the density, the structure and composition of the material. The sooner a man understands that, the better. If


TRANS. AM. CER. SOC. VOL. XVII
FIG. 5.
MODULUS OF RUPTURE OF BURNED CLAY CLAY WITHOUT GROG
MODULUS OF RUPTURE - LBS. PER SQ. IN.
CONE TEMPERATURES
27.0%
25.5%
24.5%
18.1%
FIG. 6.
MONTGOMERY & RILEY
MODULUS OF RUPTURE OF BURNED CLAY CLAY WITH 25% GROG
MODULUS OF RUPTURE - LBS. PER SQ. IN.
CONE TEMPERATURES
19.6%
16.5%
14.1%
12.8%

you put more water in your clay than necessary to form the lubricant to enable one granule to lock with another, you float the granule and separate the bond. If you go below that mark, the lubricant is not there for the granules to lock, so it is a matter of experiment for a man to ascertain the natural temper of his clay, as I stated before, which is governed by the density structure and composition of the body.

Mr. Montgomery: I might say that this work was done in order to ascertain whether small variations in water content, due to any cause whatever, would affect our finished ware. We came to the conclusion that the factory practice of judging the plasticity by feel was sufficient and that a more accurate measurement of the water was not necessary.

Mr. Stover: I would like to ask one question about the way this series of trials was carried on; was it laboratory work with the small kiln? If not, what was the size of your kiln?

Mr. Montgomery: The work was done in our laboratory, and a small test kiln was used for the burning.

Mr. Stover: Then your time in burning would hardly be parallel to the work of larger kilns in larger shops?

Mr. Montgomery: Burning in a small test kiln cannot be compared to that done in a large commercial kiln. Nevertheless, we find that we can base our factory work on our laboratory work and connect up the two very well.

Prof. Parmelee: These tests were made on one clay?

Mr. Montgomery: One clay.

Prof. Parmelee: Was that a plastic fire clay in the same sense that the New Jersey Cretaceous clays are plastic?

Mr. Montgomery: It is a first class plastic fire clay, although not as plastic as a ball clay.

Prof. Parmelee: It was a plasticity, which you do not have to develop by grinding?

Mr. Montgomery: No, pugging is sufficient.

Prof. Parmelee: Mr. Montgomery has without doubt obtained these results on the clays he has experimented with, but it is an open question as to whether his conclusions are general.

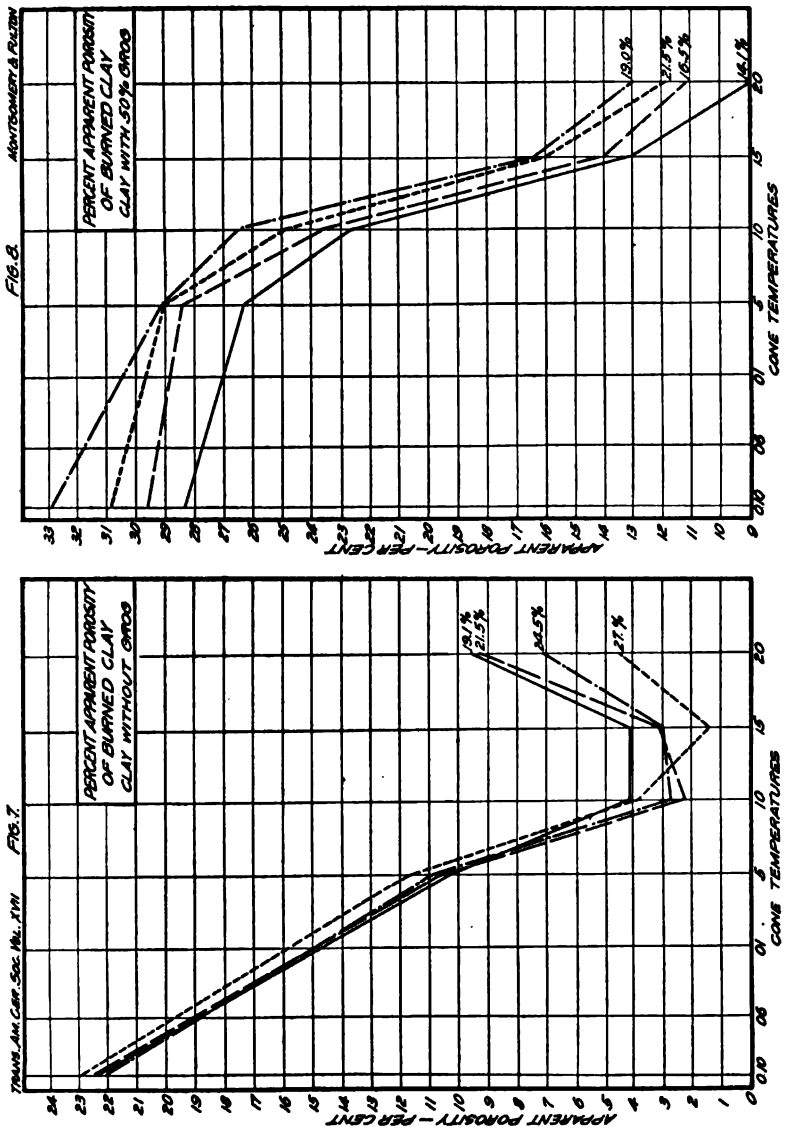


FIG. 6.
MONTGOMERY & PLOTON
PERCENT APPARENT POROSITY OF BURNED CLAY CLAY WITH 50% GROG
19.0%
21.5%
16.5%
16.1%
APPARENT POROSITY - PER CENT
CONE TEMPERATURES
FIG. 7.
TRANS. AM. CER. SOC. VOL. XVI
PERCENT APPARENT POROSITY OF BURNED CLAY CLAY WITHOUT GROG
19.1%
21.5%
24.5%
27.1%
APPARENT POROSITY - PER CENT
CONE TEMPERATURES

I think that is the difference between Mr. Purdy's experience and Mr. Montgomery's.

Mr. Purdy: That St. Louis clay has to be weathered in order to get it into the condition you desire. That differs from the New Jersey clay, but when it is weathered, it is a soft clay like the New Jersey clay.

The point I make is this: for one sagger maker, you have to have your batch a little bit more plastic than for another. I don't know whether it is a difference in strength, choice, prejudice or what, but we found, we had to temper our batches differently for the different men, and we were making slabs that carry heavy loads. At one time we had a frightful loss, due to fire clay slabs failing under load; and as some of you know, we visited a good many of our friends and asked pertinent questions regarding their experiences in the manufacture of slabs, etc., and got samples of the clays they were using. The net result of our investigation was that it did not matter so much about the clay, so long as you had a good clay, but it is important to standardize the method of manufacture all the way through the process, even through the burning. The result of our studies is a considerable length of life of our slabs, and we are using today practically the same clays we were using formerly and get at least three times the life.

The moisture content in the mixture as put through our pug mill is gauged entirely by the pugger's own experience. It is not a question of weighing the water or determining the percentage of water; we have never known how much water was in that pugged mass, never paid any attention to it, but depend on the experience of the pug man.

Mr. Yates: What difference was there between that which was perfect and that which was defective?

Mr. Purdy: It is to some extent a choice of grog. I was surprised at the fineness, to which, some ground their grog. For our large slabs, we would not use finer than 16 mesh. Our screen limits are 4 and 16 for our large slabs. What does not go through the 4, we grind over, and what goes through the 16, we use elsewhere. I noticed that Mr. Weelans made a careful selec-

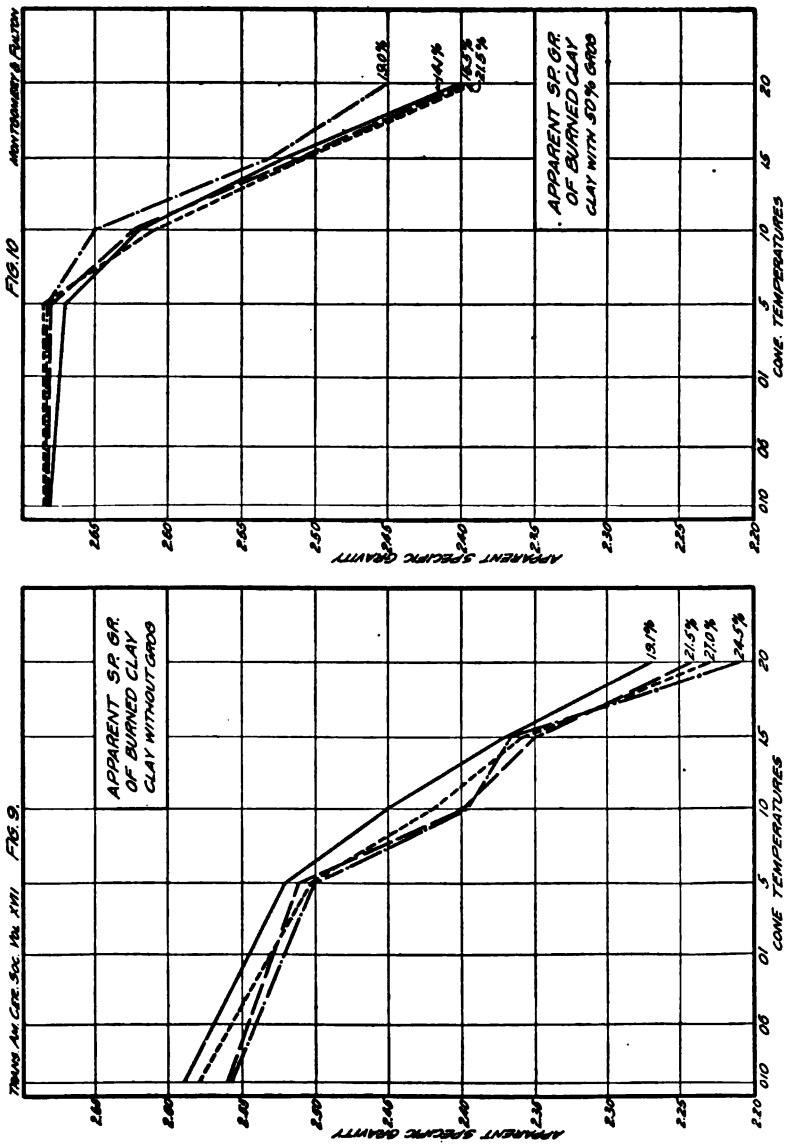


FIG. 10
MONTGOMERY & EATON
APPARENT SP. GR. OF BURNED CLAY CLAY WITH 50% GROG
18.0%
19.1%
21.5%
24.5%
APPARENT SPECIFIC GRAVITY
CONE TEMPERATURES
TRANS AM. CER. SOC. VOL. XVII
FIG. 9.
APPARENT SP. GR. OF BURNED CLAY CLAY WITHOUT GROG
19.1%
21.5%
21.0%
24.5%
APPARENT SPECIFIC GRAVITY
CONE TEMPERATURES

tion of the size of his grog. That is one very important thing that I learned in Mr. Weelans' plant.

Then, too, we believe in pugging. Our clay goes through a long horizontal pug mill, drops down into a short brick machine and is forced out through a large die. It is then put into a clay cellar which is built out in the middle of the room, in which cellar the clay is stored for at least two days. We notice that our slab makers test each piece with their thumbs to pick out the chunks they want, and we find that one man will always pick out a chunk a little softer than the other, although they are practically making equally good bats. Selection of the grog, thorough pugging and having the clay stiffer or softer to suit the man are our secrets.

Mr. Yates: Was the clay improved by making it finer or coarser? You say you changed the grog, were very particular about the grog. Did you make it finer or coarser?

Mr. Purdy: For the slabs that were to stand the greatest strain, we cut out the fines.

Mr. Montgomery: I think Mr. Purdy has said that the small variation in consistency required by different workmen does not affect the finished ware. Is that right?

Mr. Purdy: Yes.

Mr. Montgomery: That is the main object of this paper.

Mr. Purdy: But my point is this, a man can not make as strong a slab, if it is a little dryer than he wants it. It is the structural density and structural firmness developed by the man himself that is the essential thing. He has got to have that clay just right or he can not get the strength required. For a given man, therefore, you must have a given condition of plasticity. This is the benefit of a cellar, where each man can select his clay. They had to be trained to this.

Mr. Yates: I think if Prof. Purdy will keep out the "I guess" and "be gorra" and get down to the standards of the thing, there is a natural temper in each clay requiring so much water for a lubricant; if you go beyond that, you will float the granules; if you haven't sufficient water to make a mix of the

granules to form your plastic bond, the finished material will be weak and punky.

Mr. Purdy: I had not been in our plant long when our manager said, "What is a research engineer, anyhow?" I said, "A man that knows when to do things practically and when to do things theoretically." It is a happy medium between the two that the research engineer is supposed to know, and in this particular case I think we are following good scientific principles, even though we don't measure the water.

A STUDY OF FIRE CLAY, SHALE, AND SURFACE CLAY MIXTURES WITH REFERENCE TO THEIR POROSITY TEMPERATURE RELATIONS

BY G. H. BROWN[1]

Although mixtures of fire clays and shales, and fire clays and surface clays, are used to some extent in the production of structural clay products, our knowledge of the behavior of mixtures of the materials is somewhat vague.

In the testing of clays, we encounter materials which in themselves are not entirely suited to the production of the class of ware desired. We sometimes have available two types of materials, possessing widely different properties, and the question arises what will be the probable effect of mixing the two, and what are the best proportions for the mixture. Surface clays and shales are encountered which overburn readily, their vitrification ranges being too short. On the other hand, a fire clay may prove too refractory for the temperatures reached in the kiln, and the lowering of the vitrfication range by mixing with a clay maturing at a lower temperature may be desirable.

Although the exact behavior of mixtures of two clays cannot be predicted by measurements made upon one set of samples, it was thought that a study of the porosity-temperature relations of mixtures of a typical fire clay and surface clay, and a fire clay and shale, would be of value in estimating the behavior of mixtures of like materials.

Materials Used. For the investigation, a No. 2 fire clay from Kittanning, Pa., a paving brick shale from near Canton, Ohio, and a surface clay from near Groveport, Ohio, were selected. The burning behavior of the clays may be judged from their temperature-porosity curves, shown in Figures 1 and 2.

Preparation of Test Pieces. The clays were dried at 110°C. and then ground to pass a 12 mesh sieve. Eighteen mixtures

[1] By permission of the Director, Bureau of Standards.

were prepared, nine containing fire clay and shale in varying proportions and nine containing fire clay and surface clay. Each mixture was wedged on a marble slab, until it acquired consistency favorable to molding by the stiff-mud process, and then pressed into briquettes 2 in. by 1⅛ in. by ⅝ in. on a hand repress machine. The briquettes were dried at room temperature and finally in a drying oven at 110°C.

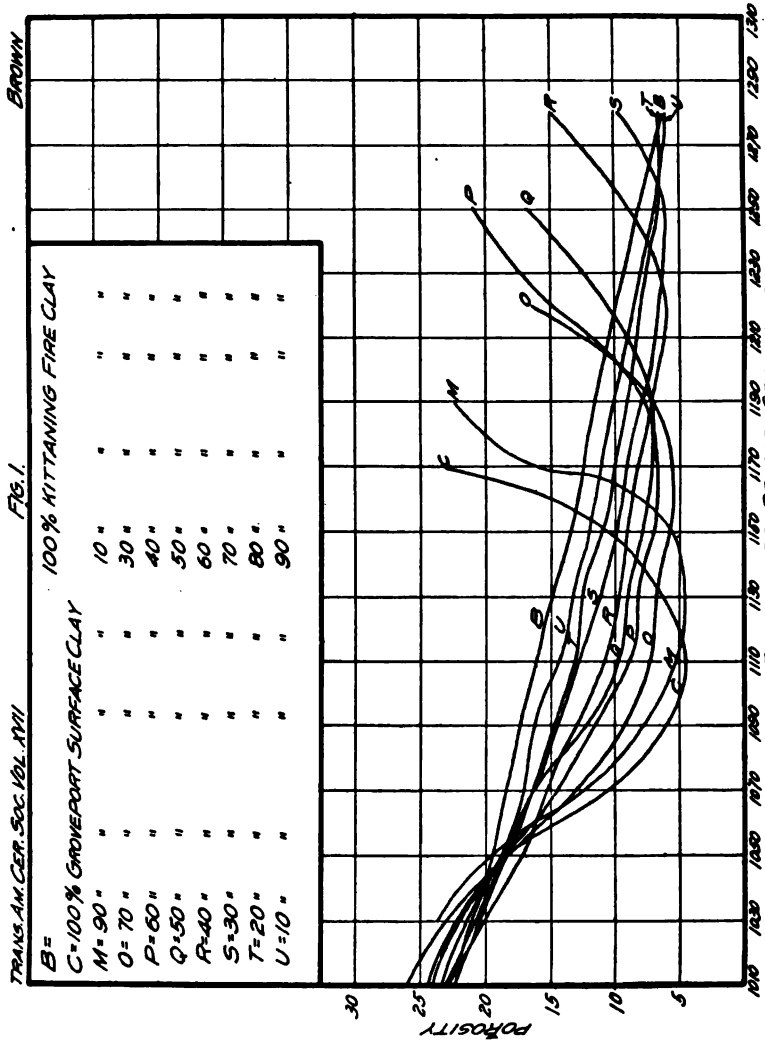
Burning. The test pieces were burned in a gas-fired test kiln, the temperature of the kiln being increased uniformly at the rate of 25°C. per hour after reaching 850°C. The test pieces from each mixture were drawn from the kiln at 20° intervals, starting at 1010°C., the burn being completed at 1280°C.

The porosities of the burned pieces were determined in the usual manner, and the porosity-temperature curves plotted as shown in the figures.

Fire Clay–Surface Clay Mixtures. In a study of the curves, we must take into consideration the fact that the mixtures were wedged only, and that the results would be very different if intimate grinding in ball mills had been employed. We may say that the mixing was about equal to that which the clays would receive in preparation for manufacture by the stiff-mud process in commercial practice.

The porosity-temperature relations of the fire clay-surface clay mixtures are plotted in Fig. 1. In the diagram, Curve C represents the porosity-temperature relations of the surface clay, and Curve B the porosity-temperature relations of the fire clay. Curve M indicates the behavior of a mixture of 90 percent surface clay and 10 percent fire clay, Curve O the behavior of a mixture of 70 percent surface clay and 30 percent fire clay, and so on, Curve U being the porosity-temperature curve of the mixture of 90 percent fire clay and 10 percent surface clay.

It will be noted that by the addition of ten percent fire clay to the surface clay, the temperature at which over-burning or vesicular structure develops is raised from 1110°C. to 1150°C. The vitrification range of the mixture is somewhat superior to that of the surface clay, the mixture showing but slight change in porosity over a temperature interval of 40°C.


TRANS. AM. CER. SOC. VOL. XVII
FIG. 1.
BROWN
B =
C = 100% GROVEPORT SURFACE CLAY
M = 90 " " " 10 " " " "
O = 70 " " " 30 " " " "
P = 60 " " " 40 " " " "
Q = 50 " " " 50 " " " "
R = 40 " " " 60 " " " "
S = 30 " " " 70 " " " "
T = 20 " " " 80 " " " "
U = 10 " " " 90 " " " "
100% KITTANING FIRE CLAY
POROSITY
30
25
20
15
10
5
1010
1030
1050
1070
1090
1110
1130
1150
1170
1190
1210
1230
1250
1270
1290
1310
TEMPERATURES - DEGREES CENTIGRADE

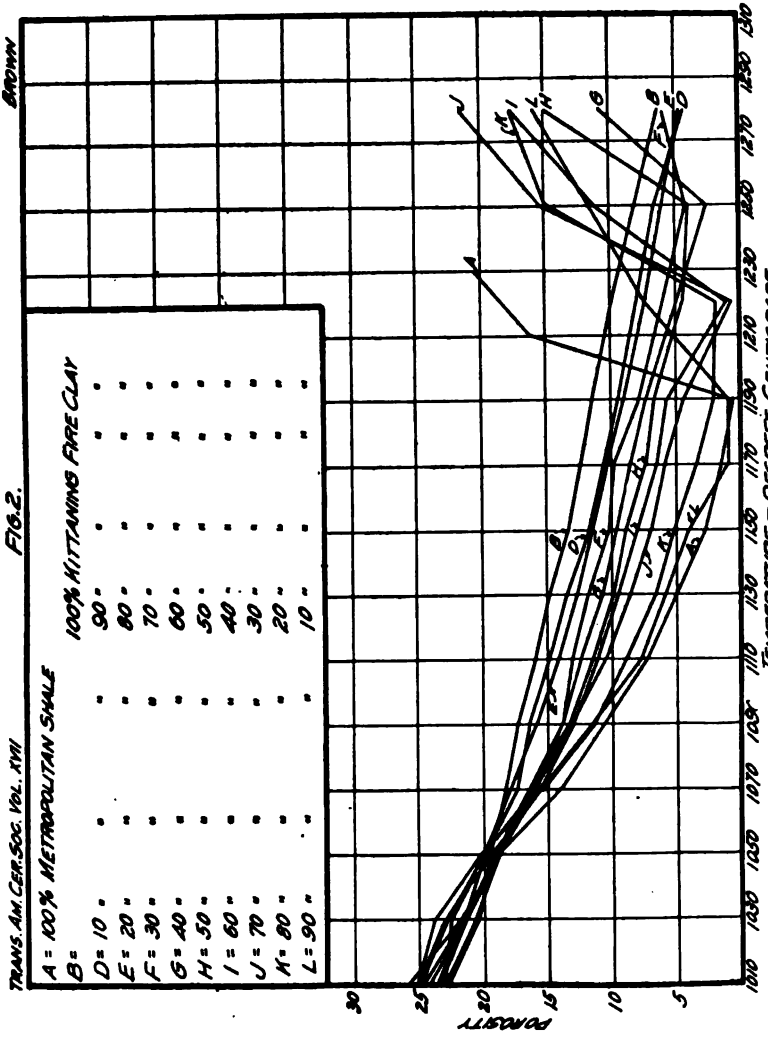
The addition of 30 percent fire clay to the shale appears to raise the temperature at which overburning takes place to 1170°C., although the vitrification range is very similar to that of the ten percent mixture.

Increasing amounts of fire clay in the mixture appear to further raise the temperature of overburning, although the minimum porosities are higher than in the low fire-clay mixtures. It will also be noted, that, with increasing amounts of fire clay in the mixture, the porosity-temperature curves show a tendency to become more nearly parallel, and a more regular decrease in porosity with increase in temperature is in evidence.

We may say, therefore, that by the addition of fire clay to the surface clay in varying amounts, the characteristic tendency of the surface clay to overburn is not destroyed, although the temperature at which a vesicular structure develops is increased. We may say, that additions of from 10 to 40 percent fire clay to the surface clay improves its burning behavior by increasing the vitrification range. On the other hand, additions of surface clay to the fire clay in amounts of 10 to 40 percent improve the burning behavior of the latter. Thus, if we were burning ware molded from the fire clay to a porosity of 10 percent at 1230°C., by the addition of 10 percent of the surface clay we may attain the same porosity, 10 percent, by firing to 1190°C., or by firing to the same temperature or cone, we attain a porosity of 8 percent and ware of correspondingly greater strength.

Fire Clay–Shale Mixtures. The porosity-temperature relations of the fire clay-shale mixtures are plotted in Fig. 2.

Curve A represents the porosity-temperature relations of the shale and Curve B those of the fire clay. The behavior of this series of mixtures is very similar to that of the fire clay-surface clay mixtures. The tendency of the shale to overburning is in evidence throughout the series, although the temperature at which a vesicular structure develops is higher with increasing amounts of fire clay. A slight improvement in the vitrification behavior of the shale is noted with the addition of 10 and 20 percent of fire clay, although the improvement is somewhat offset by the increase in temperature necessary to secure it. As in the case


TRANS. AM. CER. SOC. VOL. XVII
FIG. 2.
BROWN
A = 100% METROPOLITAN SHALE
B = 100% HITTANING FIRE CLAY
D = 10 " 90 "
E = 20 " 80 "
F = 30 " 70 "
G = 40 " 60 "
H = 50 " 50 "
I = 60 " 40 "
J = 70 " 30 "
K = 80 " 20 "
L = 90 " 10 "
POROSITY
TEMPERATURE - DEGREES CENTIGRADE

of the fire clay-surface clay mixtures, additions of shale to the fire clay cause decrease in porosity when firing to the same temperature, or the same porosity may be attained by firing to a lower temperature.

Conclusions. Where shales or surface clays are mixed with fire clays, the impure clays appear to retain their characteristic tendency to overburning, although the temperature of overburning increases with decreasing amounts of the impure clays in the mixtures. It must again be emphasized, that the mixtures herein reported are somewhat similar to those secured in blending clays for stiff-mud manufacture, and that intimate grinding of the mixtures would afford different data.

Additions of fire clay to surface clays or shales in amounts from 10 to 30 percent appear to improve the vitrification behavior of the impure clays, although an increase in burning temperature is necessary.

Additions of surface clay or shale to a fire clay tend to decrease the porosity when firing to the same temperature.

DISCUSSION

Prof. Orton: It seems to me, that this paper has a good deal of meat in it for the practical clay manufacturer who has a clay of unsatisfactory characteristics and is trying to better it by mixture. Certainly, many manufacturers of crude clay products, whose clays do not work to suit them, have tried to doctor them with some other clay. As far as I am aware, it has not been pointed out so clearly heretofore, what the effect of such additions of one clay to another clay really is. I remember one of my own early experiences in clay manufacture, when I tried to improve the refractoriness of the shale that I was using for paving brick by additions of a fire clay. I put in about 30 percent of this fire clay at some considerably increased cost per 1000 of brick manufactured, but I could not see that I made any improvement at all in my results. The fineness of grinding, which we would naturally do for commercial paving brick, was such that the two materials didn't blend much. It seemed that

the 30 percent of fire clay grains were scattered about in a matrix composed of 70 percent of the grains of the shale. The fire clay broke up the continuity of the shale body and caused it to give a poorer rattler test than it did before, but it did not change the essential characteristics of the actual matrix material. Since that time, I have had opportunity to study the effect of blending clays, where it is possible to approach more nearly to real blending, in which case, each clay is reduced to slip form in which the particles are individual mineral grains and not aggregates. In a mixture of two slips, something approaching a new clay is produced, which will be approximately the mean between the two components in its properties, but it has not been found possible under ordinary commercial conditions to blend fire clays and shales and get very much benefit from the blend. I have seen the thing tried in a good many different places, under a good many different conditions with poor success. Mr. Brown has brought that out here, that in such blends, each clay retains its own characteristics to a startling degree, and, if one clay has a bad vitrification behavior, even a small quantity of it mixed with the other will still show that peculiarity.

Prof. Staley: It may be that I did not read the curves right, or I did not hear what Mr. Brown said, but I thought that the paper proved just the reverse of what Prof. Orton says the curves show. As I understand it, the paper demonstrates that you can increase the vitrification range or increase the temperature to which a clay can be burned, without causing overburning, and that the properties of the mixture correspond pretty well to the percentages of the ingredients. As far as blending clays in the Iowa district is concerned, they do blend clays quite commonly. They blend fire clays and surface clays to make a clay which will vitrify at a lower temperature, and they blend surface clays with shales and increase the vitrification range. They blend clays in all proportions and go to a good deal of expense to do the blending. They certainly would not do that, if they got no benefit. I know of one plant that was considered a failure, could not operate at all; there they are hauling 20 percent of another clay or shale, something like 40 miles to blend with a surface

clay they have at the plant, and they have turned the plant from a failure into a commercial success.

Prof. Orton: Mr. Chairman, it may be that I did not make myself clear. The point, which attracted my attention in the curves in Mr. Brown's paper, is the fact that one material shows a certain abrupt change of its properties in overfire. Now, if you add some of the other clay, the mixture still shows this same characteristic overburn behavior, and, if you add more, you still find it through the entire series. Each clay keeps its individuality in the mixture.

Regarding the commercial possibilities of blending clays, I would not want to be understood as claiming it is not possible to blend some clays commercially, because it is being done all the time. The point I want to make is, that if your materials are similar in nature the blend is more successful, but if the materials are of markedly diverse character, and especially, are used in a coarsely ground condition, you will find that the matrix material, in predominance, will define the character of the mass, and the grains of the other will damage the mixture by being either immature or overfired.

Mr. Yates: I don't think there is much difficulty in blending clays, if you take a fire clay of a not too siliceous body that is plastic. If it is of a high siliceous nature, it won't blend; you have got to get two clays suited to each other, but if you want a strong plastic clay, the fire clay is much stronger than the shale. If you have shale that is weak and contains more or less alkali that will break down the body of the silica, you add to it, the fire clay for the refractory part of your material, so it is just a question whether you want plasticity or refractory material. If you want your goods to stand up in the kiln, you have got to have a relative relation between your two clays, before you can bring them together, but you can get a much stronger brick by the use of fire clay mixed with shale, provided you get them both adapted to each other in structure.

DATA ON THE EFFECT OF PRESSURE APPLIED TO A DUST BODY

BY CULLEN W. PARMELEE

The experiments previously undertaken on the effect of pressure applied to clay in the plastic condition[1] led us naturally to the study of pressure upon material containing a smaller amount of water. There appears to be scant information available regarding this topic. The only item which has come to our attention is a short article in the *Collected Writings* of Herman Seger, page 805.

The clays which we used were two of the sort which are typical of those mined in Middlesex County, New Jersey, and are employed in the manufacture of terra cotta, stoneware, sanitary ware and similar articles. The clay designated as No. 33 was of the same lot as used in the experiments previously referred to. The No. 9 clay contains less sand. It burns to a denser body than the No. 33 clay, otherwise it is very similar.

These two clays were pulverized to pass a 40 mesh sieve and then moistened sufficiently to cohere as a lump when squeezed in the hand. The moisture content of each was determined. Clay No. 9 was found to contain 11.4 percent water, while clay No. 33 had 7.1 percent water. The clays, therefore, contained the amounts of water within the limits characteristic of dust bodies, which ranges from 8 to 15 percent.

The clays were stored in tight receptacles for a time to permit an equalizing of the moisture content, and they were kept in these tight receptacles at all times to insure uniformity.

The clay test pieces were made in a die bored through with a cylindrical shaped opening 5.3 cm. in diameter. A tightly fitting plug closed the bottom and a long tightly fitting plug served as a plunger. The die was placed upon the bed plate of a 100 000 pound Riehle compression testing machine, and a weighed quantity of the clay was introduced into the die. Similar quantities were used for Numbers 6 to 24½ and equal quanti-

[1] Vol. XVI, *Trans. Amer. Cer. Soc.*

ties for Numbers 25 to 45. The amount of the compression load applied was, of course, under complete control of the operator.

We found that with clay No. 33, water appeared about the base of the die when the compression load was 30,000 pounds. Water and clay oozed out when more than 10,000 pounds was applied to clay No. 9.

TABLE I—CLAY No. 9

NOS.	POUNDS	TOTAL VOLUME	SOLID VOLUME	TOTAL POROSITY[1]	OPEN PORES[1]	SEALED PORES[1]
				percent	*percent*	*percent*
25	2000	32.52	26.57	22.39	21.03	1.36
26	2000	32.87	25.99	26.47	22.93	3.54
27	4000	30.75	25.96	18.45	12.86	5.59
28	4000	31.73	27.11	17.04	16.67	0.37
29	5000	30.93	28.21	16.67	12.62	4.05
30	5000	30.86	26.66	15.75	12.67	3.08
31	10000	29.07	26.21	10.91	6.25	4.66
32	10000	15.18	13.81	9.92	5.72	4.20
33	10000	29.32	26.27	11.61	7.61	4.00
34	20000	29.41	27.22	14.38	9.13	5.25
35	20000	29.65	26.15	13.38	8.60	4.78
36	20000	29.52	26.29	12.28	8.29	3.99
37	20000	29.09	27.09	7.38	5.94	1.44
38	30000	29.37	26.37	11.36	8.22	3.14
39	30000	28.43	25.91	9.71	6.44	3.27
40	40000	28.26	25.54	10.65	5.55	5.10
41	40000	29.18	26.65	9.49	8.55	0.94
42	50000	28.86	27.37	5.44	3.61	1.83
43	50000	28.62	26.02	9.99	6.18	3.81
44	75000	26.73	24.24	10.27	4.95	5.32
45	75000	26.99	24.28	11.16	3.13	8.03
31A	75000	26.99	24.43	10.48	5.52	5.58

[1] Calculated in terms of solid volume.

The effect of increasing pressure was quite apparent in the appearance and the hardness of the trials. The drying shrinkages measured along the diameter of the pieces was not affected. The shrinkages as measured through the thicknesses of the pieces show no regular changes which may be attributed to the effect of compression.

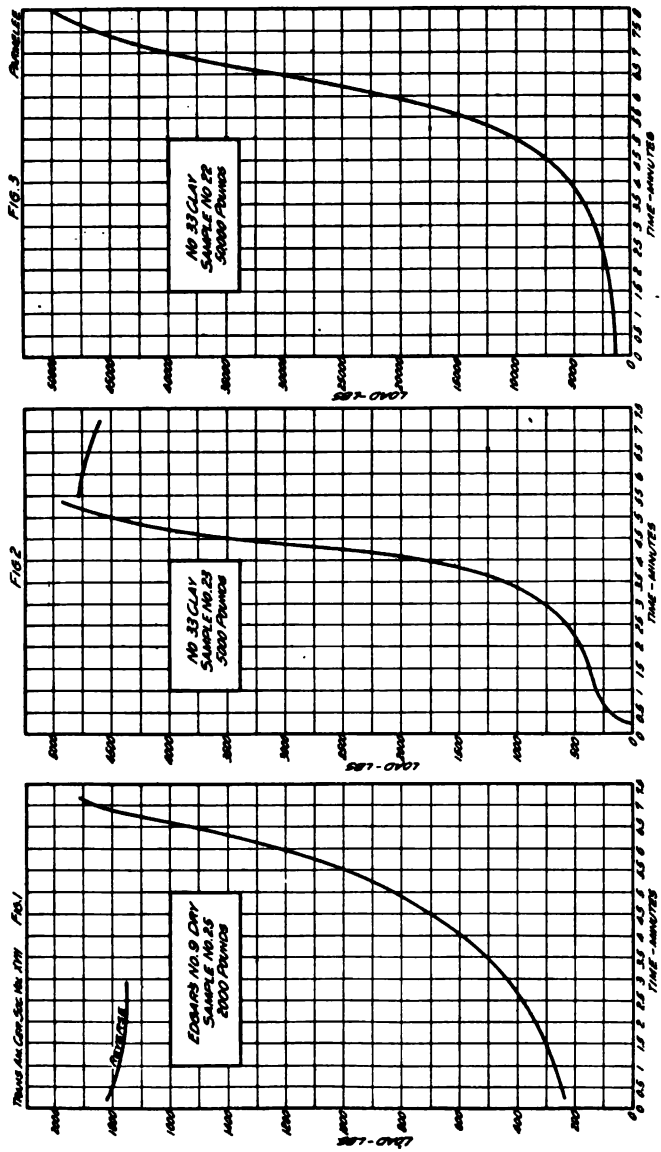


FIG. 3
NO 33 CLAY
SAMPLE NO 22
50000 POUNDS
FIG. 2
NO 33 CLAY
SAMPLE NO. 23
5000 POUNDS
FIG. 1
EDGAR'S NO. 9 DRY
SAMPLE NO. 25
2000 POUNDS
TIME - MINUTES
LOAD - LBS

The manner in which the clays take up the loads is shown in Figures 1, 2 and 3. The points, through which these curves are drawn, were obtained by reading the time intervals at which the various loads were applied. The two short detached curves (one is marked "reverse") on Figures 1 and 2 show how the loads on the test pieces fall away after the maximum load has been

TABLE II—CLAY No. 33

NOS.	POUNDS	TOTAL VOLUME	SOLID VOLUME	TOTAL POROSITY[1]	OPEN PORES[1]	SEALED PORES[1]
				percent	*percent*	*percent*
2	2000	40.17	27.09	48.28	46.91	1.37
11	2000	46.05	31.91	44.32	.....	....
3	3000	41.27	29.75	38.70	38.15	.55
12	3000	44.05	30.34	45.18	41.89	3.29
4	4000	43.99	30.68	43.38	41.85	1.53
13	4000	44.05	31.46	40.05	40.05	.00
5	5000	45.32	32.56	39.19	38.02	1.17
14	5000	43.06	30.59	40.76	37.85	2.91
14½	5000	43.28	31.14	38.98	38.37	0.61
24	5000	43.13	31.16	38.86	38.12	0.74
24½	5000	42.59	31.41	35.59	35.68	0.91
6	10000	41.66	31.31	33.05	33.08	0.00
7	20000	36.14	27.91	29.48	27.19	2.29
16	20000	39.87	31.25	27.58	27.32	0.26
8	30000	35.08	28.14	24.66	23.45	1.21
17	30000	39.39	31.41	25.40	25.30	0.10
9	40000	35.42	28.10	26.05	24.91	1.14
18	40000	39.25	30.99	26.65	25.16	1.49
10	50000	35.39	28.27	25.17	25.00	0.17
19	50000	38.89	31.38	23.93	23.77	0.16
22	50000	38.51	30.62	25.76	22.99	2.77
20	75000	38.64	31.82	21.43	22.40	....
1	100000	33.64	26.93	24.91	23.06	1.85
21	100000	38.02	31.03	22.52	21.59	0.93

[1] Calculated in terms of solid volume.

applied, and before any attempt was made to release the load on the trial pieces. This is not due to the oozing of the clay nor the water about the piston in the die because similar phenomena were observed when dry coarse sand and dry ground flint were separately tried under the same conditions. This falling off of the

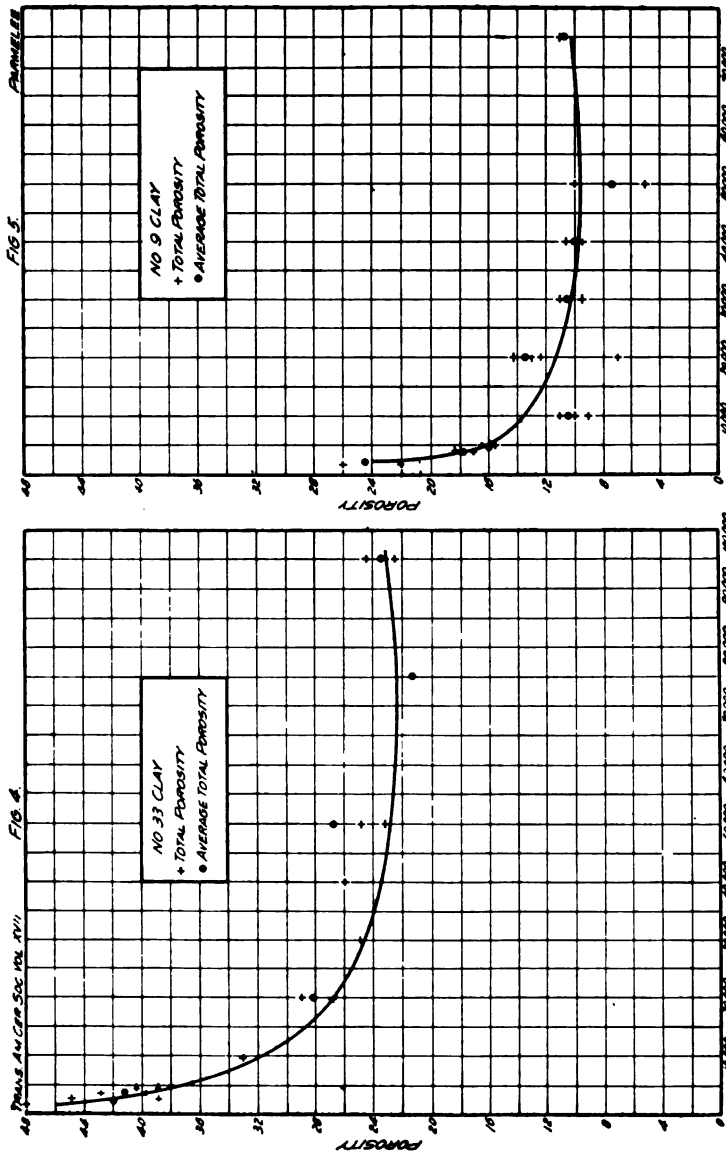


FIG 5.
NO 9 CLAY
+ TOTAL POROSITY
● AVERAGE TOTAL POROSITY
POROSITY
PRESSURE - POUNDS
FIG 4.
NO 33 CLAY
+ TOTAL POROSITY
● AVERAGE TOTAL POROSITY
POROSITY
PRESSURE - POUNDS

load is probably due to a shifting of the granular particles of material or to a crushing of the grains under the pressure.

After compression, the trial pieces were burned in a coal-fired kiln to cone 5. Clay No. 33 showed no indications of vitrification, while the trial pieces from clay No. 9, when broken, had a gloss and a conchoidal fracture as well as a much greater hardness. With increase of pressure the trial-pieces of clay No. 33 show a very marked increase in resistance to scratching or cutting. Measurements of the pieces across the faces as well as in the direction from which the pressure was applied show a slight decrease of shrinkage with increase in pressure.

Determinations were made of the total volume of the trials, the volume of the open pores and the true specific gravity, *i. e.* specific gravity of the solid. From this data we have calculated the total volume of the pores, the volumes of the open pores and the volumes of the sealed pores in terms of the volume of the solid. These results are shown in Tables I and II.

We have plotted the results thus obtained with reference to co-ordinate axes, one of which indicates changes of pressure, the other represents changes in porosity. Drawing a curve through these points we have the results shown in Figures 4 and 5.

From these curves, it is apparent, that as the pressure is applied, there is a rapid increase in the density of the trial pieces until a certain point is reached. After that, an increase in pressure does not produce a proportionate, or even a material, increase of density.

THE RELATION BETWEEN THE MODULUS OF ELASTICITY AND THE POROSITY OF BURNED CLAY[1]

BY A. V. BLEININGER AND G. H. BROWN

In work done several years ago, it was thought desirable to study the stress-strain relation of clay specimens burned to several temperatures. The modulus of elasticity, such an important constant for steel and other materials, has not been known with any degree of exactness for different classes of clays burned to various degrees of hardness.

Seven clays were selected for this work and made up on a small auger machine into test bars having the dimensions 3½ by 3½ by 12 inches. Each clay was burned to from six to eight temperatures, varying between cone 08 and cone 5. The ends of the bars were ground parallel.

The extensometer gauge length was six inches, and the deformation under compression was determined by means of a screw micrometer apparatus with telephone attachment, which permitted of making readings to 0.0001 inch. The testing machine used was an Olsen apparatus of 200 000 pounds capacity.

The raw materials used were the following clays:

No. 32, a No. 2 fire clay from Kittanning, Pa.

No. 33, a No. 2 fire clay from Nelsonville, Ohio.

No. 34, paving brick shale from Galesburg, Ill.

No. 35, paving brick shale from Canton, Ohio.

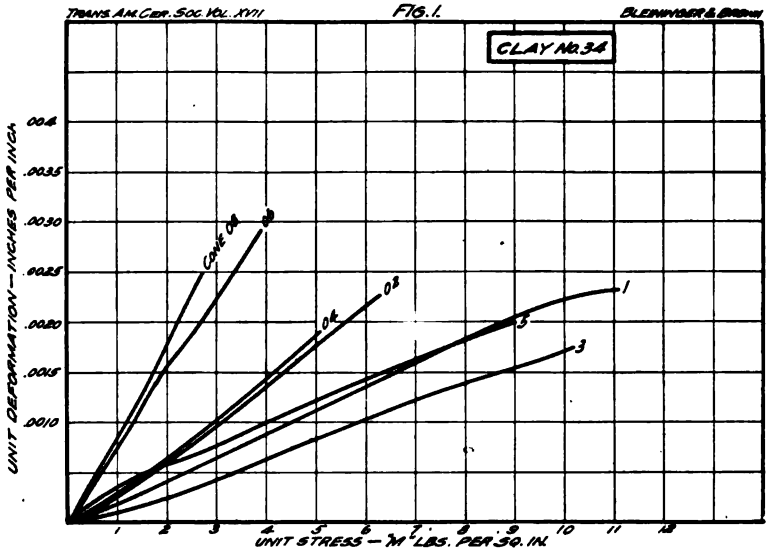
No. 37, calcareous surface clay, Chicago, Ill.

No. 38, red burning surface clay, Urbana, Ill.

No. 40, ferruginous shale, Cleveland, Ohio, used for making building brick.

To clays No. 37 and 38, Ottawa standard sand was added to the amount of 50 percent.

[1] By permission of the Director, Bureau of Standards.


TRANS. AM. CER. SOC. VOL. XVII
FIG. 1.
BLEININGER & BROWN
CLAY No. 34
UNIT DEFORMATION — INCHES PER INCH
.004
.0035
.0030
.0025
.0020
.0015
.0010
CONE 08
08
04
02
1
3
5
1 2 3 4 5 6 7 8 9 10 11 12
UNIT STRESS — M LBS. PER SQ. IN.

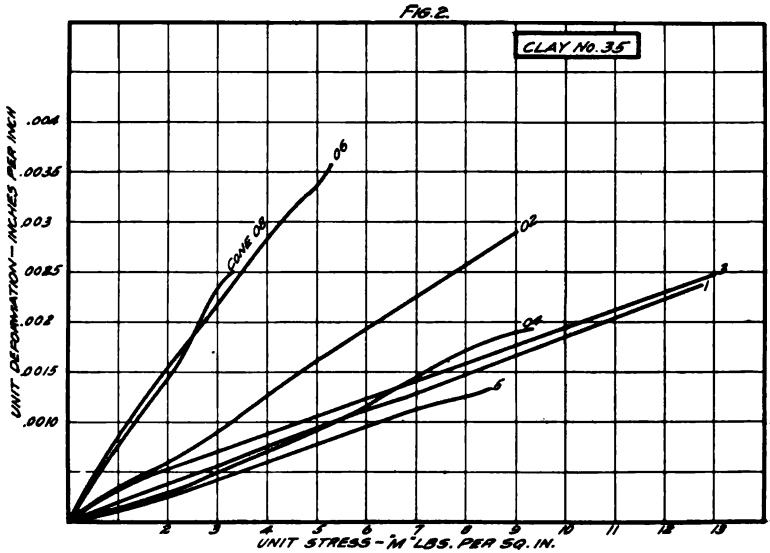
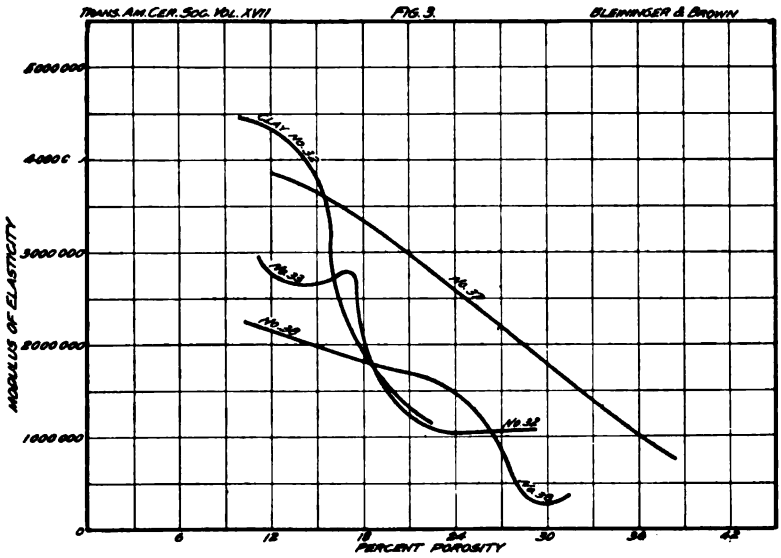


FIG. 2.
CLAY No. 35
UNIT DEFORMATION — INCHES PER INCH
.004
.0035
.003
.0025
.002
.0015
.0010
06
CONE 06
02
3
1
04
5
2 3 4 5 6 7 8 9 10 11 12 13
UNIT STRESS — M LBS. PER SQ. IN.

Before making the modulus tests, the porosity of the specimens was determined by the usual method.

Results of Modulus Tests. The stress-strain curves of two materials, the two shales, No. 34 and 35, are plotted in the diagrams of Figs. 1 and 2. It was not considered necessary to reproduce all of the curves, since these two represent quite fairly their general behavior. It will be observed at once that the inflexion point of the elastic limit practically fails to appear. This is due in part to the brittle nature of the material, to the giving way of the clay along the lamination planes and to flexure of the bar. The curves also show minor departures from the linear relation and show discontinuities which must likewise be ascribed to the causes just mentioned. Referring to Fig. 1, it is at once evident that the deformation coefficient decreases as a function of the increasing closeness of the material. In other words, the unit deformation for unit stress, say, 1000 pounds per square inch, becomes less and less as the maturing temperature rises. Since the modulus of elasticity is obtained by the relation, $s \div d$, where s=stress and d=unit deformation, it is evident that the modulus increases with the burning temperature, and the tangents of the angles of the deformation curves are inversely proportional to the modulus. Thus with the burning temperature of cone 08 and 06, the deformation is comparatively large for relatively small pressures, but decreases with the higher fired bodies and approaches a minimum value, that corresponding to cone 3. It is interesting to note, that overburning, at cone 5, again increases deformation due to vesicular structure. The modulus of elasticity ranges from 1,344,000 to 5,828,000. The curves of Fig. 2, clay No. 35 (shale), agree very closely with No. 34. An exception from the general relation is noted in the case of the specimen burned at cone 3, which shows a slightly greater deformation than those fired at cone 1. Since this shale is not readily overburned at the temperature in question, no explanation of this divergence can be offered. The modulus rises from 1,485 000 to 6,400,000. The latter figure is very high, but appears to be characteristic for soundly vitrified brick of the grade used for the manufacture of paving brick.


TRANS. AM. CER. SOC. VOL. XVII
FIG. 3.
BLEININGER & BROWN
MODULUS OF ELASTICITY
5000000
4000000
3000000
2000000
1000000
0
CLAY No. 37
No. 37
No. 39
No. 38
No. 32
No. 33
6
12
18
24
30
36
42
PERCENT POROSITY

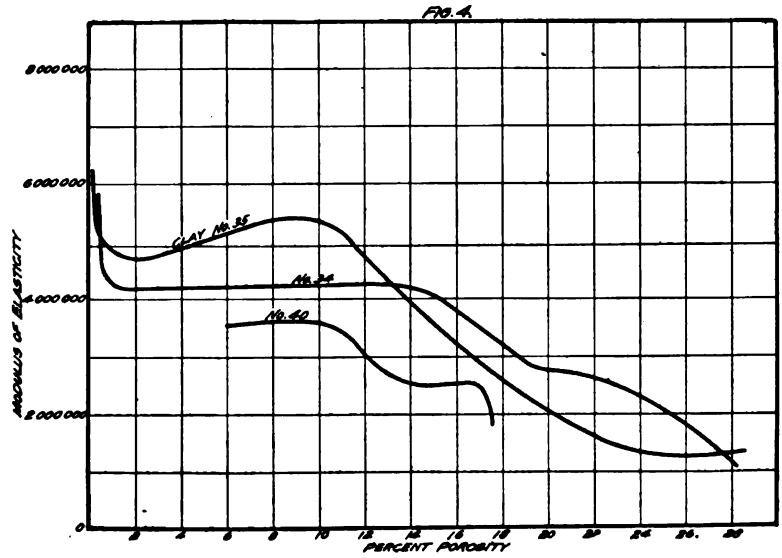


FIG. 4.
8000000
6000000
4000000
2000000
0
MODULUS OF ELASTICITY
CLAY No. 35
No. 34
No. 40
PERCENT POROSITY

Compiling the moduli for the several materials, we have the following results:

CLAY	MINIMUM MODULUS	MAXIMUM MODULUS
No. 32	1,194,000	4,531,000
No. 33	1,152,000	3,000,000
No. 34	1,344,000	5,828,000
No. 35	1,485,000	6,400,000
No. 37	847,000	3,750,000
No. 38	375,000	2,250,000
No. 40	1,937,000	3,563,000

If now we plot the cotangents of the angles of the curves as shown in Figures 1 and 2 for all of the clays against the porosities corresponding to the several burning temperatures, we shall obtain the relation between the modulus of elasticity and the porosity. This has been done in Figures 3 and 4. In the nature of the case it cannot be expected that smooth curves can be made to express such a relation. This is due principally to the fact that the porosity of the specimens is not uniform throughout the entire cross section but is lowest near the exterior, increasing towards the center of the piece, and that the structure planes due to lamination cause distortion of an irregular nature. For this reason only broad generalizations can be deduced from the curves.

Considering the diagram of Fig. 3, representing the No. 2 fire clays and the surface clays, it is observed that the Kittanning clay approaches a very much higher modulus than the Nelsonville material and appears to be more consistent in its behavior. The irregularity of clay No. 33 as shown by the upper part of the curve cannot be explained. The uniform increase in the value of the modulus for the Chicago clay is somewhat surprising. In this connection, it must be remembered that the material was well prepared and contained 50 percent of sand. The Urbana surface clay was somewhat handicapped, in spite of the sand admixture, by its sticky colloidal nature, which caused it to be subject to lamination and a tendency to check. The Chicago material, on the other hand, showed but little lamination and

dried well. The main point to be brought out is, of course, the fact that, in general, the modulus is a function of the porosity of the material and that, according to its nature and previous treatment, each clay has its own characteristic porosity-modulus curve. In the diagram of Fig. 4, representing the shales, points have been obtained closer to zero porosity than in the preceding figure. It seems to be characteristic of shales, that the modulus of elasticity increases gradually from the point of maximum porosity, remains practically constant during the later interval of vitrification and rises rapidly as complete vitrification is reached.

The marked difference in the value of the modulus in favor of paving brick shales calls attention to the several proposals to be found in the literature concerning the application of a function of this factor in estimating the toughness of the materials. According to Johnson,[2] "the area of the stress diagram up to the elastic limit, divided by the volume of the specimen under test is a measure of the ability of the material, per unit volume, to absorb and give out energy or to resist shocks without injury; and the total area of the stress diagram is its measure to resist a single blow without rupture." Martens[3] makes the statement: "By comparing the proportional elongation (or compression) to maximum stress with the final elongation (or compression) after the rupture, the ratio of development of total toughness of the material could be determined if of practical value."

Acknowledgments are due Messrs. R. K. Hursh, now of the University of Illinois, and J. G. Bragg, for carrying out the laborious experimental part of the work.

DISCUSSION

Mr. Swalm: May I ask whether the vitrified body would have more tenacity than a fire clay body of the same porosity?

Mr. Bleininger: This is not a question of tenacity.

Mr. Swalm: Elasticity, I should say.

Mr. Bleininger: Yes, there would be quite a difference in favor of the vitrified body.

[2] J. B. Johnson, *The Materials of Construction*, p. 81.
[3] *Handbook of Testing Materials*, Vol. I, p. 304.

Mr. Purdy: May I ask for a definition of terms here? By vitrified Mr. Swalm means porcelain. Do you not?

Mr. Swalm: Yes.

Mr. Purdy: He wants to know if porcelain is stronger than fire clay.

Mr. Bleininger: As a rule, maximum strength and maximum modulus coincide.

Mr. McMichael: Your results, Mr. Bleininger, seem to bring out the point, in regard to paving brick, that while the strength increases very rapidly, with an increase of maturing temperature, the elasticity decreases, so that to get the maximum combined strength and toughness, you would burn somewhat below the maximum temperature.

Mr. Bleininger: Yes.

Mr. McMichael: That checks with my own observation.

Mr. Bleininger: In the diagram overburning is shown by the curve dropping again; in other words, the deformation increases and hence the modulus decreases.

NOTE ON THE SILICA BOND IN SAND-LIME BRICK[1]

BY W. E. EMLEY, A. A. KLEIN AND E. M. SANBORN

It is generally accepted by all who have investigated the subject, that the bonding material in sand-lime brick is a hydrated calcium silicate, formed by the action of lime on finely divided silica, under the influence of high pressure steam. A scientific investigation of this material should lead to results which would be of great importance technically. Thus a study of its properties should enable us to predict the action of weather on the brick; a study of the conditions under which it is formed should throw some light on the relative efficiencies of different methods of manufacture; and it might be possible to develop some method of analysis, by which the exact amount of silicate present in a brick could be determined.

In an article on the "Chemistry of Sand-lime Brick," published in the *Transactions*, Vol. XIII, p. 648, T. R. Ernest attempted to deal with this particular silicate in a scientific manner. The work was published in greater detail by Parr and Ernest, *Bull. No. 18*, Illinois State Geological Survey. It was, therefore, decided to use their work as a starting point for further investigation. Of course, the first step necessary was to make sure that their experimental methods were correct, and that their conclusions were justified by the results obtained. Unfortunately, a careful study of their methods has brought to light errors which render many of their conclusions untenable.

They prepared a number of samples, by treating mixtures of pure hydrated lime and precipitated silica with high pressure steam, and then attempted to analyze, by the following methods, the compound formed:

(1) Treat the mass with a dilute solution of hydrogen sulphide, to dissolve the excess of free lime.

(2) The total lime remaining is regarded as combined in the form of silicate.

[1] By permission of the Director, United States Bureau of Standards.

(3) A treatment of the compound with dilute acid, followed by dilute alkali, under certain prescribed conditions, will dissolve the calcium silicate. A determination of the silica in the solution shows the amount in combination with the lime.

(4) The residue remaining undissolved is regarded as an excess of free silica.

Hydrogen sulphide was adopted as the solvent agent for the free lime after an apparently extended investigation, including the use of acetic acid and phenol. We have experimented with all of these materials, and fail to find any of them satisfactory for the purpose. For example, a sample of calcium silicate was treated with hydrogen sulphide until no trace of free lime could be detected by means of the microscope. Further treatment of the same sample resulted in the further solution of lime. Indeed, we find that this calcium silicate is so readily hydrolyzed that the calcium can be leached out indefinitely by water alone. Any attempt to dissolve the free lime must therefore result in a partial decomposition of the silicate, no matter how weak the acid used.

The method of separating the soluble and insoluble silica is approximately accurate only when the insoluble material is present in the form of comparatively large and unhydrated grains. Such was not the case in these experiments, so that it is highly probable that some of the silica, reported as combined, was really free.

The determinations of combined lime and silica, when calculated to molecular proportions, showed ratios varying from .818 $CaO \cdot SiO_2$ to 1.30 $CaO \cdot SiO_2$. From this data, the authors conclude that the major portion of the bonding material in sand lime brick is $CaO \cdot SiO_2$. The discrepancies in the results are accounted for by the assumption of other silicates, such as $2\,CaO \cdot SiO_2$, or $CaO \cdot 2\,SiO_2$. On consideration of the inaccuracies in the method of analysis noted above, it is improbable that the conclusion as to the presence of silicates other than the one to one, is justified. This is further emphasized by the fact that the average of their own analyses shows a ratio of .992 $CaO \cdot SiO_2$.

Parr and Ernest also attempted to determine the water combined with the silicate, by the following method: Dry the

sample at 100°C., to drive off the free water. The total loss on ignition of this dried sample is the combined water.

The futility of attempting to drive off the free water from an amorphous calcium silicate by heating it to 100° needs no further notice. The total loss on ignition includes not only the water combined with the silicate, but also, undoubtedly, some water combined with the lime as calcium hydroxide, and the carbon dioxide from the calcium carbonate, the presence of which it is almost impossible to prevent.

The results obtained led Parr and Ernest to the conclusion that the calcium silicate probably forms no definite hydrate. The evidence advanced can hardly be considered conclusive either for or against this statement.

In their petrographic examination of the synthetic compounds, and of sand-lime brick, Parr and Ernest have made use of thin sections only. It has been repeatedly shown that the constitution and quantitative optical properties of the compounds can be determined only by the use of immersed grains. On all slides examined, they observed small highly doubly-refracting crystalline particles, which, in line with their previous assumption of complex silicates, they believed to be zeolitic. Particles answering this description are uniformly present in all samples examined, and we have identified them as calcium carbonate.

OXIDE OF LEAD vs. CARBONATE OF LEAD IN GLAZES

BY ARTHUR S. WATTS

To the ceramist who has the manufacture of lead bearing glazes in his charge, the subject of lead pigment as a glaze ingredient should receive careful consideration. Few men who have this matter in charge are conscious of the material saving which is possible by substituting one of the oxides of lead for the double salt which has come into almost universal use in ceramic operations.

The lead compounds most readily adaptable to ceramic uses are the following:

Litharge	(PbO)	yellow oxide of lead.
Minium	(Pb_3O_4)	red oxide of lead.
White Lead	($2\,PbCO_3+Pb(OH)_2$)	carbonate of lead.

In the glass or glaze, the lead exists always in one form—PbO. Hence, any additional oxygen or other elements present in the pigment are only added expense and, provided the cost of all the pigments were the same, lowered content of PbO would make the pigments other than PbO more expensive. Litharge (PbO) contains 12.7 percent more lead than does white lead, and minium Pb_3O_4 contains 10.6 percent more lead than does white lead. The increased use of white lead has been accounted for in three ways:

1. For many years the red lead and litharge of commerce were not sufficiently pure to insure a lead glaze of uniform quality, while commercial white lead gave satisfactory results.

2. White lead was obtainable in a much finer state of pulverization than either red or yellow lead oxide and caused less trouble from settling of the glaze.

3. The white lead was sold at times for slightly less, owing to its lower metal content.

The prices prevailing January 28, 1915, were as follows:

Litharge, ton lots, 5⅛c. per pound; car lots, 5c. per pound.

Minium, ton lots, 5⅝c. per pound; car lots, 5½c per pound.

Lead carbonate, ton lots, 5⅛c. per pound; car lots, 5c. per pound.

The above statement is based on the assumption, that the use of the oxides of lead manufactured at the present time does not introduce any difficulties other than those encountered in the use of carbonate of lead.

To justify this assumption, a number of commercial glazes were prepared with PbO introduced in each of the three forms. The glazes containing litharge (PbO) are indicated by the numeral I, those containing minium are indicated by the numeral II, and those containing lead carbonate are indicated by the numeral III.

The type of glazes are as follows:

Type A. Soft Raw Lead Jardiniere Glaze.

$$\left.\begin{matrix} 0.60\ PbO \\ 0.10\ K_2O \\ 0.15\ CaO \\ 0.15\ ZnO \end{matrix}\right\} 0.15\ Al_2O_3 \left\{ 1.5\ SiO_2 \right.$$

Matures at cone 02.

Composition

I	II	III
Litharge ...48.23	Minium 49.38	Carbonate of lead 55.85
Potash feldspar...20.04	Potash feldspar...20.04	Potash feldspar...20.04
Whiting 5.40	Whiting 5.40	Whiting 5.40
Zinc oxide .. 4.38	Zinc oxide .. 4.38	Zinc oxide .. 4.38
China clay .. 4.65	China clay .. 4.65	China clay .. 4.65
Flint 17.30	Flint 17.30	Flint 17.30

Type B. Soft Fritted Wall Tile and Art Pottery Glaze.

$$\left.\begin{matrix}0.40\ PbO\\0.10\ K_2O\\0.25\ Na_2O\\0.25\ CaO\end{matrix}\right\} 0.2\ Al_2O_3 \left\{\begin{matrix}1.5\ SiO_2\\0.5\ B_2O_3\end{matrix}\right.$$

Matures at cone 02.

Frit

$$\left.\begin{matrix}0.5\ Na_2O\\0.5\ CaO\end{matrix}\right\} \begin{matrix}1.0\ SiO_2\\1.0\ B_2O_3\end{matrix}$$

Frit Composition

		Raw		*Melted*
0.5 Borax	× 382 =	191.0	× 202 =	101.0
0.5 Whiting	× 100 =	50.0	× 56 =	28.0
1.0 Flint	× 60 =	60.0	× 60 =	60.0
		301.0		189.0

Glaze Composition

I	II	III
Litharge 33.40	Minium 34.20	Carbonate of lead ...38.65
Melted frit..31.63	Melted frit..31.63	Melted frit..31.63
Potash feldspar...20.81	Potash feldspar...20.81	Potash feldspar...20.81
China clay .. 9.66	China clay .. 9.66	China clay .. 9.66
Flint 4.50	Flint 4.50	Flint 4.50

Type C. Hard Raw Lead Jardiniere Glaze.

$$\left.\begin{matrix}0.25\ PbO\\0.20\ K_2O\\0.35\ CaO\\0.20\ ZnO\end{matrix}\right\} 0.25\ Al_2O_3 \cdot 2.00\ SiO_2$$

Matures at cone 4.

Composition

I	II	III
Litharge 20.43	Minium 20.92	Carbonate of lead....23.64
Potash feldspar ..40.72	Potash feldspar ..40.72	Potash feldspar ..40.72
Whiting 12.82	Whiting 12.82	Whiting 12.82
Zinc oxide .. 5.93	Zinc oxide .. 5.93	Zinc oxide .. 5.93
China clay .. 4.72	China clay .. 4.72	China clay .. 4.72
Flint 15.38	Flint 15.38	Flint 15.38

Type D. Fritted White Ware Glaze. (Boric Acid Frit.)

$$\left.\begin{matrix}0.25\ PbO\\0.15\ K_2O\\0.05\ Na_2O\\0.45\ CaO\\0.10\ ZnO\end{matrix}\right\}\ 0.25\ Al_2O_3\ \left\{\begin{matrix}2.0\ SiO_2\\0.4\ B_2O_3\end{matrix}\right.$$

Frit

$$\left.\begin{matrix}0.10\ Na_2O\\0.90\ CaO\end{matrix}\right\}\ 0.1\ Al_2O_3\ \left\{\begin{matrix}1.0\ SiO_2\\0.8\ B_2O_3\end{matrix}\right.$$

Frit Composition

	Raw	*Melted*
0.1 Borax	$\times 382 = 38.2$	$- \times 202 = 20.2$
0.9 Whiting	$\times 100 = 90.0$	$- \times 56 = 50.4$
0.6 Boric acid	$\times 124 = 74.4$	$- \times 70 = 42.0$
0.1 China clay	$\times 258 = 25.8$	$- \times 222 = 22.2$
0.1 Flint	$\times 60 = 60.0$	$- \times 60 = 60.0$
		194.8

Glaze Composition

I	II	III
Litharge 19.37	Minium 19.85	Carbonate
Melted frit..33.87	Melted frit..33.87	of lead ...22.43
Potash	Potash	Melted frit..33.87
feldspar ..29.00	feldspar ..29.00	Potash
Zinc oxide .. 2.82	Zinc oxide .. 2.82	feldspar ..29.00
China clay .. 4.49	China clay .. 4.49	Zinc oxide .. 2.82
Flint 10.43	Flint 10.43	China clay .. 4.49
		Flint 10.43

All the glazes studied were placed upon porous wall tile and upon semi-vitreous individual butters. Each glaze was fired at the temperature for which it was designed. The glazes of each type were made up with the same water content, so that the amount of glaze applied was as nearly uniform as possible. The glaze containing the carbonate of lead was thus thicker, when applied, but contained the same amount of glaze-forming material.

Regarding the mechanical behavior of the different glazes, it is worthy of note, that the glazes containing litharge form a dense coating upon drying, and no tendency to dust is noticed in handling the glazed ware before firing. A tendency to dust is apparent in the glazes containing minium and very pronounced in the glazes containing carbonate of lead. This tendency to dust displayed by glazes containing white lead is known to all white ware potters, while old glaze-makers agree that the trouble was practically unknown in the glazes containing litharge.

The choice of litharge for clear glazes upon red and buff bodies has been based upon the opinion that a clearer, more liquid glaze is obtained than with an equal equivalent of carbonate of lead. In commercial glazes of this type, the use of white lead appears to give a faint opacity not apparent when litharge or minium is used. The impression prevails that litharge produces a glaze with a faint yellow cast which is decreasingly ap-

parent when minium and carbonate of lead are used. In the glazes tested, this tendency is apparently distinguishable but is so slight that it could be disputed.

As to the fluidity of the glazes with the different pigments, there is a pronounced decrease in flow with decrease of Pb content in the pigment used, although the same amount of PbO is present in each glaze.

In conclusion: This study indicates that, as regards fluidity, the lowest PbO content is possible where the PbO is introduced as litharge, the increase being very slight where minium is used and quite appreciable where lead carbonate is used. Just what these ratios are, has not been determined and would probably be different for different glazes.

The tint imparted by litharge is not sufficient to condemn it in any of the glazes tested. In the cone 4 glazes, the tint imparted is not invariably distinguishable even by an expert. The difference in tint, when minium and when lead carbonate is used is not distinguishable in either the cone 02 or the cone 4 glazes.

As regards surface texture, the difference in effect of equal molecular equivalents of litharge, minium and lead carbonate is quite distinct, and varies from a glassy, highly polished effect with litharge, to a faint egg-shell effect with lead carbonate. The use of minium gives an effect intermediate but rather nearer that obtained from the use of litharge.

As regards crazing, glaze A has not crazed either on tile or dinner ware after a period of four weeks. This glaze was designed for cone 02, but samples were also fired at cone 4, and these have not crazed after four weeks.

Glaze B, designed for cone 02 fire, crazes on both tile and dinner ware at cone 02 but when fired at cone 4 shows no evidence of crazing on either ware after four weeks.

Glaze C, designed for and fired at cone 4, shows no evidence of crazing when applied either to wall tile or dinner ware after a period of four weeks.

Glaze D, designed for and fired at cone 4, shows no evidence of crazing after four weeks either on wall tile or table ware.

A period of four weeks is insufficient to prove whether a glaze will craze, but later records will be obtainable on these trials.

DISCUSSION

Prof. Binns: I did not hear the first remarks of Prof. Watts and I do not know whether he mentioned anything about the mechanical behavior of litharge and white lead respectively in dipping.

Mr. Watts: I did not mention anything. I will say, however, that in all the glazes made with litharge you get a glaze which goes on the ware and holds tight; that is, there is no tendency to dust. With the Pb_3O_4, there is a slight tendency to dust and, as soon as the glaze becomes dry, the ware must be handled with a great deal of care. In the use of white lead, every potter knows that he has to use considerable care in handling the glazed biscuit, that is, the unfired biscuit after it is glazed, because the white lead glaze dusts off very readily. Whether or not the disinclination of the red lead and the yellow lead to dust off the ware would have a sufficient advantage to encourage their use, I do not know, but I do know that there is a very marked difference in their behavior in that way.

Prof. Binns: I was referring more particularly to the floating properties in dipping; do not the litharge and red lead show a tendency to settle and not remain floating?

Mr. Watts: No, they did not in this investigation, but my litharge and red lead were both in a very fine state of subdivision, much finer than we used to get when I was manufacturing lead glazes.

Prof. Binns: I do not know whether Prof. Watts is acquainted with the form of litharge that comes on the market.

Mr. Watts: I used a commercial litharge, a very finely ground product.

Prof. Binns: I want to know whether the white lead was analyzed?

Mr. Watts: Yes, the white lead was analyzed, and the other leads were analyzed. I haven't the analysis of the lead here.

Prof. Binns: There was no evidence of adulteration?

Mr. Watts: No, they were all very clean products, but they were selected with the idea of getting a good product, and the people who furnished them said they were the same as they furnished to the regular market. I don't think that we are confronted with the difficulty that we used to experience in buying lead and materials of that sort. The lead market is at the present time controlled by two or three large concerns, I think not over three and they are large enough concerns so that I think the chance of adulteration would be small, except perhaps a small content of zinc or some other metal of that kind which might be in any commercial product.

Mr. Silverman: I should like to ask Mr. Watts whether he thinks that the difference might possibly be due to the heat taken up in the molecular dissociation of the carbonate, a condition which you do not face with the oxide? If all three substances are fired equally and for the same length of time, a part of the heat applied will be used in breaking up the lead carbonate and red lead before they serve as a flux. Would that account for your difference?

Mr. Watts: No, I don't believe it could; the enormous amount of waste heat in any process like a ceramic process would be such, that I don't believe the small amount which would be taken up in a case of that sort would really have anything to do with it. Furthermore, the fact that I took these soft glazes and fired them to six cones higher than the normal temperature without any evidence of change as to their relative physical behavior would indicate that the physical property displayed by the white lead was something other than that.

Mr. Silverman: Then the white lead behavior continues even after prolonged heat?

Mr. Purdy: Let us have that question again.

Mr. Silverman: My question is whether, if three pieces are fired for the same length of time at the same heat, the heat re-

quired for dissociation of the white lead and red lead might not cause a difference in fusion as compared with litharge.

Mr. Mayer: I want to ask Mr. Watts what particular kind of oxide he was using?

Mr. Watts: Picher.

Mr. Mayer: I have used the Picher Company's litharge about three months at a time and found no difficulty with the use of the lead and no particular advantage. There is a slight advantage in price, but no difference in the dipping, no difference in any way at all. We used it for, I think, altogether about four months and got equally good results as we did with red and white lead; no better results, but at that time we were having possibly an excessive amount of pinholes. Now I have stopped the use of the lead on that account. When I went back again to white lead, it disappeared. Whether the cause of that was this oxide of lead, I cannot tell for sure, but I can say this about it. that I am going to take the matter up again because there is a saving in cost, there is no question about that. But I have noticed no difference in color and no difference in dipping or in any way at all from what there was over the white lead. Of course, I refer particularly to that new form of litharge we are getting now which is a very light powder and very different from the old form of litharge that we used to get.

Mr. Watts: I want to refer to the point made with regard to dusting. I do not think the amount of litharge in most whiteware glazes is sufficent to cause enough cementing action to be the cause of any difficulty. I was able to rub off with an ordinary cheap cotton glove all the glaze that was on the foot of each piece, so that I could test the piece in the kiln without any difficulty. With regard to the point Mr. Mayer made on pin-holing, I don't think anything about the pin-holing with regard to different leads, but I want to bring out as strongly as possible the fact, that I got invariably more fluxing action where I used one molecular equivalent of litharge than where I used one molecular equivalent of lead carbonate, and that was the point referred to by Mr. Silverman. I cannot explain that, but it seems to be a point worthy of consideration.

Prof. Binns: Mr. Watts stated that the leads were analyzed; does that mean analyzed simply for impurities? Was the litharge correctly estimated as to its content of metallic lead?

Mr. Watts: Oh yes, the amount of PbO was determined, and the amount of other metal constituents was determined.

Prof. Binns: Was there any metallic lead present?

Mr. Watts: There was no evidence of that.

Prof. Binns: Some study was conducted a while ago by one of the students with whom I am connected, on the action of lead silicates, and we found it extremely difficult to procure litharge free from metallic lead. If it contains metallic lead, that would account for its action and also for pin-holing.

CLASSIFICATION OF FLOOR TILES AS RELATED TO DEGREE OF VITRIFICATION

BY FORREST K. PENCE

The tile industry of this country had its beginnings in those states where clay deposits of the red and buff burning type alone were to be found. For some years, these local clays only were utilized, and the process of manufacture being in a stage of experiment and development, the quality of the tiles naturally reflected the crudity of the early methods.

Plain tiles of simple outlines were made in colors obtained from the natural color of the clay as developed in the fire. The range of colors was limited to those obtained by blending of red and buff burning clays, and a modification of the clay color through addition of oxide of manganese. These tiles were used with or without a glaze coating.

In case a glazed tile was desired, a transparent glaze was applied to the colored clay body, the color of the glazed tile being determined by the color of the body. Such tiles were listed as "plain glazed." The same kind of bisque tiles were also sold for use in floors and listed as "plain unglazed." Thus tiles were early divided into plain glazed and plain unglazed classes, the term plain conveying the idea of simple or undecorated.

Time has witnessed marked change and divergence from these early lines of tile manufacture. A demand for variety in glaze colors led to the introduction of coloring agents into the glaze. Thus instead of deriving its color from the body, the glaze by its own ingredient color was intended to obscure and overcome the color influence of the body. This gave rise to that class of glazed tiles known as "enamels," so called because the glaze obscured the body. However, these colored glazes could not be classed as enamels according to the accepted ceramic application of the term enamel.

In later years, there has been a very great development of types of glazed tiles, classification of which it is not the function of this paper to discuss.

In the case of floor tiles, the plain unglazed type, being in general of that porous nature that made it adapted to the application of a glaze when desired, has been succeeded by two general classes known as "vitreous" and "semi-vitreous." This has resulted from an effort to produce tiles that would be approximately non-absorbent and of far greater durability than the floor tiles of earlier manufacture.

When feldspars, ball clays, and china clays were utilized in the blending of floor tile bodies which were fired at high temperatures, the vitreous or practically impervious tile became a reality. Into these blends have been introduced the coloring oxides adapted to high temperature development, as cobalt oxide, chromium oxide, etc., for production of a line of vitreous colors constituting the white and colored vitreous tiles of to-day.

There yet remains, however, a field for those tiles whose color is produced by the development in the fire of the natural color of the clay composition. The colors obtained are peculiar to these clays, and an attempt to duplicate the color quality of the reds, buffs, etc.. by use of coloring oxides in vitreous body composition would be commercially impracticable. The best color development of these clays is obtained before the body structure, characteristic of the vitreous tiles, is reached. In fact, an attempt to obtain the vitreous structure by firing these clays to higher temperature will, in general, result in overfire, giving a tile of inferior quality and durability.

It has been possible, however, by making proper selection of clays and by using improved methods of preparing the clays, as well as in pressing and firing the tiles. to produce from the basis of red and buff clay composition a class of tiles which approach the vitreous in their quality of low absorption. These are comprised in the semi-vitreous class and, in connection with the vitreous tiles, have taken the place of the old plain unglazed type.

In addition to the two general classes of floor tile on the market to-day there are special classes which should be noted. Probably the most prominent of these would be quarries which, in process of manufacture and character of product, bear closer

relation to well made stiff-mud brick than to the regulation floor tile. It may be noted, also, that ordinary brick is often applied to uses that would logically require tiles.

Then there are floor tiles made to meet certain artistic demands, such as tiles with surface designs inlaid with glazes or vitreous slips, or in some cases tiles with the entire surface glazed. In this same connection there are also on the market, tiles of peculiar crudity of outline and open body structure, which might properly be classified under the old type of plain unglazed. An example of this type is the so-called Moravian tiles in which a porous body is used either glazed or unglazed.

In the tile business, mosaics are also considered as a separate group, although the small tiles used in the various mosaic designs would individually belong in the vitreous and semi-vitreous classes.

There has already been pointed out the need of a legal definition of vitrification as applied to clay ware.[1] In the same paper the phenomena of vitrification is discussed.

In the case of floor tile, custom has made use of the term **vitreous** instead of **vitrified**, probably because the former term was thought to place more emphasis upon the dense or glassy structure of the tile. In the same way, the term **semi-vitreous** has been applied to denote a marked development of vitreous structure.

The term "plain unglazed" has become almost obsolete in this country, although some confusion has arisen from the application of the term to vitreous and semi-vitreous tiles, because they, in a sense, correspond to the descriptive meaning of the words. However, as applied to tile classification, "plain unglazed" must denote that early group of bisque tiles that were used, either glazed or unglazed, or tiles corresponding thereto.

So in the tile industry, there is need of a clear understanding of these terms and a basis of classification that will eliminate the uncertainties, arising from attempts at classification on the basis of opinion.

[1] Orton, *Trans. Amer. Cer. Soc.*, Vol. XVI, p. 496.

The absorption test because of its practicability has become the accepted method of determining degree of vitrification.

Since various methods of determining absorption have been used and proposed,[2] a preliminary investigation was made to determine which method seemed most satisfactory. For this purpose, six tiles were selected and absorption determined by various methods. The tiles were thoroughly dried before each determination, and distilled water was used throughout to prevent error through deposit of salts. The methods for obtaining absorptions were as follows:

A—Boiled one hour, soaked twenty-four hours.

B—Boiled three hours.

C—Soaked forty-eight hours.

D—Soaked forty-eight hours, one surface (the face) exposed.

In A, B, and C, tiles were completely immersed.

The results given in the order of their determination, are shown in Table I, in which the figures express absorptions in terms of percent of the dry weight of the tile:

TABLE I

	RED_1	RED_2	$BUFF_1$	$BUFF_2$	$BLUE_1$	$BLUE_2$
A.....	3.29	3.11	5.16	6.60	0.004	0.0025
B.....	3.19	3.16	4.90	6.37	0.0025	0.002
C.....	2.28	2.00	4.50	5.93	0.0035	0.0015
D.....	2.51	2.26	5.00	6.05	0.004	0.0015

The above results were considered in connection with the practicability of the operations involved, in forming a conclusion as to the method preferred.

The three hour boiling method involves weighing of tile taken direct from boiling water, an operation which is unsatisfactory.

The method of soaking while completely immersed, without boiling, is open to the objection of being conducive to the im-

[2] O'Connor, Vol. XV, 254. Orton, Vol. XVI, p. 511.

prisonment of air. This is demonstrated in the preceding table, in which the figures for C, with one exception, are lower than those obtained by the other methods.

The method of soaking with one surface exposed would appear to increase the likelihood of error because of the influence of amount of surface exposed. the difficulty in case of curved surfaces, and the variable extent to which the tile may project above the water. However, a comparison of C and D in Table I, shows that the opportunity for capillary action gave substantial increase in absorption.

The method of boiling for one hour and soaking for twenty-four, the tile being completely immersed at all times, provides a process of breaking up the enclosed air followed by the operation of a soaking which allows the water to penetrate during the cooling period. A more complete absorption is obtained thereby as shown by higher figures for A in the preceding table.

In the case of a refined product like flooring tile, it is particularly necessary that the method used should combine ease of duplication with a minimum of error. On this basis, the method of one hour boiling and twenty-four hours soaking was adopted and was used in obtaining all figures for absorption that appear in following tables.

In determining what limits of absorption should define the given classes of floor tiles, a number of tiles were selected, at random, from each class, and their respective absorption obtained. The tiles selected were such as are regularly recognized and accepted in commercial practice, as belonging to the class to which they are assigned.

Table II shows results of determinations made on a variety of vitreous tiles. In each case, absorptions were obtained on six tiles of like character, denoted by A, B, C, D, etc., and different groups of same color denoted by No. 1 and No. 2. The figures given to the third decimal place were obtained from tiles small enough to permit weighing on a chemical balance. Those of two decimal figures were obtained from larger tiles and weighed on a torsion balance. Averages in all cases were computed to the third decimal figure.

TABLE II

	NO.	A	B	C	D	E	F	AVERAGE
White...	1	0.005	0.005	0.004	0.002	0.000	0.002	0.003
White...	2	0.00	0.00	0.00	0.00	0.00	0.03	0.005
Blue....	1	0.000	0.000	0.002	0.002	0.002	0.002	0.001
Blue....	2	0.00	0.00	0.00	0.00	0.00	0.00	0.000
Gray....	1	0.012	0.008	0.005	0.005	0.006	0.005	0.007
Gray....	2	0.00	0.00	0.00	0.00	0.00	0.00	0.000
Green...	1	0.008	0.051	0.041	0.020	0.029	0.026	0.029
Green...	2	1.93	2.18	2.14	1.65	1.55	1.77	1.870
Pink....	1	1.68	1.93	1.14	0.75	1.51	1.81	1.470
Pink....	2	0.006	0.004	0.002	0.007	0.003	0.006	0.005
Cream..		0.00	0.00	0.03	0.00	0.00	0.00	0.005

Since the figure denoting upper limit of absorption for vitreous tile must also be the lower limit for semi-vitreous, it is necessary to consider the absorptions obtained from both classes in order to establish a dividing line between them.

The absorption figures for the semi-vitreous tiles, determined in the same manner as for the vitreous, are shown in Table III.

TABLE III

	NO.	A	B	C	D	E	F	AVERAGE
Black.....	1	5.05	3.82	4.53	4.48	3.56	4.58	4.34
Black.....	2	4.14	4.77	3.36	4.31	4.30	5.16	4.34
Red.....	1	4.34	4.16	3.46	4.03	4.31	4.09	4.06
Red.....	2	2.49	2.76	3.02	4.09	2.97	2.93	3.04
Salmon.....	1	4.15	4.73	4.40	4.86	4.43	4.51	4.51
Salmon.....	2	5.15	4.55	4.23	4.45	4.37	5.17	4.65
Buff.....	1	9.84	9.08	9.90	8.85	9.73	9.34	9.46
Buff.....	2	6.69	6.15	5.76	5.97	5.98	5.94	6.08
Chocolate.....	1	2.92	3.28	3.19	3.18	3.24	3.12	3.16
Chocolate.....	2	3.25	3.86	3.38	3.17	3.33	3.21	3.37
Light Gray.....	1	8.27	8.40	8.04	8.81	6.55	6.54	7.77
Light Gray.....	2	4.14	4.69	3.56	4.37	4.30	4.50	4.26
Dark Gray.....	1	6.96	8.27	6.55	7.08	4.99	6.47	6.72
Dark Gray.....	2	4.39	3.14	3.27	4.43	3.36	3.25	3.64

A comparison of the maximum average figure (1.870), obtained from vitreous tiles, with the minimum average figure obtained from semi-vitreous tiles indicates that their dividing line lies between two and three percent. An absorption of two percent appears rather high for vitreous tiles, but, in adopting a limit we must include all tiles of this class. If certain specifications require tiles that pass certain tests, as, the ink test, the abrasion test, etc., then it is simply a matter of tiles of the vitreous class passing these tests.

Competition between manufacturers in appealing to discriminating tastes of architects and others has led to the use of the ink test for certain tiles, particularly white, while in case of pink, where uniformity of product is not so generally obtained, and also in case of dark colors, a greater latitude in porosity is permitted, as shown by the table.

In the case of White No. 1 and White No. 2 of table for vitreous, an application of red ink to the surface of these tiles was readily removed by cold water, leaving no stain. To satisfy curiosity, six tiles of this same type, showing slight ink stain and likewise six tiles showing pronounced ink stain, were selected and absorptions determined. See Table IV.

TABLE IV

	A	B	C	D	E	F	AVERAGE
White Slight Stain.....	0.013	0.066	0.037	0.041	0.014	0.027	0.033
White Pronounced Stain...	0.273	0.129	0.190	0.057	0.798	0.785	0.372

Any general classification, however, must include all tiles commercially listed as vitreous, and the figures of table for vitreous tiles are offered as representing the commercial extreme in absorption for these tiles.

In table for semi-vitreous, absorption on single tile as low as 2.49 is obtained while minimum average absorption is 3.04. The lower limit of two percent would, therefore, not be un-

reasonable for this class. On this basis, an absorption of two percent is proposed as the figure for dividing vitreous and semi-vitreous.

The maximum average absorption obtained for semi-vitreous is 9.46. The figures, in general, are much lower and only in two cases exceed six percent. In defining this class and distinguishing it from the class to which the old term "plain unglazed" may be applied, the results indicate that an absorption of ten percent should be taken as the upper limit for semi-vitreous class. This would also be a logical lower limit for the plain unglazed class.

In this connection, absorptions were obtained in same manner as before on two so-called Moravian tiles, taken as being representative of the class "plain unglazed." Resulting percentages were 15.05 and 15.90.

As a matter of interest, absorptions were also obtained on quarries of two representative types. The resulting percentages on three quarries of first type were 8.85, 8.52, and 8.69. On two quarries of second type, the resulting percentages were 2.30 and 2.17, thus indicating that, on basis of absorption, tiles of this general character would belong in the semi-vitreous class.

In connection with the figures offered in this paper report of tests made by O'Connor[3] are of interest and give support to our conclusions.

Although figures herewith submitted are not extensive, the absorptions were obtained from groups of tiles representative of the commercial ranges and, taken in connection with the known commercial practice, justify the following as a proper basis for classification of floor tiles not obviously belonging to a special type.

The class to which floor tiles shall be assigned shall be determined by the amount of water they will absorb. Absorption shall be determined by immersing the tile in boiling water for one hour, followed by soaking in the same water for twenty-four hours. Average results shall be obtained from no

[3] *Trans. Amer. Cer. Soc.*, Vol. XV, p. 254.

less than five tiles and shall be expressed in terms of percentage of the dry weight. Classes of tiles shall be defined by the amount of absorption as follows:

Absorption—zero to two percent—vitreous

Absorption—two to ten percent —semi-vitreous

Absorption—ten or more percent—plain unglazed

VERITAS FIRING DISC

BY ROSS C. PURDY

In the discussion of a paper of this same title by Bleininger and Moore in Vol. XVI of these Transactions, a statement was made by me that the Veritas Firing Discs were made of pottery material, that is, they were made of such material as a potter would ordinarily use in the manufacture of china. I had no intentions at that time of stating that they were made of the Cook china body, for I knew very well that they were not. The statement I made was, that they were made on the premises of the Cook Pottery Company, and very likely of the same materials as they use. It developed in the discussion last year, and in correspondence since, that others are misconstruing the statement made to the effect that it was of the Cook pottery body. It is important, therefore, that all the emphasis possible should be placed upon the fact as stated, that is, that these bodies are not of the Cook pottery china bodies, but are composed of such materials as a potter would use in the construction of a china body.

The point I tried to emphasize was, that any potter could, with his own materials, make discs that, perhaps, would serve his purposes better than the standard discs manufactured by the Veritas Firing System Company. This is exactly the case at the Norton Company. Our ware is such, that it is far from being feasible to use the discs as prepared by the Veritas Firing System Company, and if we were to install this system as a means of following our kilns, we would not want anything but the apparatus used. We would compound our own discs.

The intimation last year on the floor, and a positive statement made in conversation in the lobby were to the effect, that these rings contained magnesia, thus giving them a peculiar shrinkage behavior, and making them of more value than a ring composed entirely of pottery body materials. The following analysis shows that this disc does not contain magnesium oxide, or any other oxide not ordinarily found in pottery bodies:

	Percent
Aluminium oxide	20.98
Ferric oxide	1.18
Silica	67.48
Titanium oxide	0.40
Calcium oxide	0.44
Magnesium oxide	Trace
Sodium oxide	0.43
Potassium oxide	1.69
Loss on ignition	6.80

The above analysis is not given as key to the possible composition of these rings, for the analyses of the raw materials are not known. The only value in these analyses is the determination that no unusual ingredient is present, and that these discs are composed entirely of clay, feldspar and flint.

The writer wants to add his testimony to many others concerning the great value of this system in firing kilns. Too little attention has been paid to the proper rate of burning. The brick makers have long since learned to go slow during the oxidation period, and have learned that between the oxidation and the real vitrification period is the time to make speed. It is true that there are clays with which we can go at a rapid rate from the start of burning to the finish. but these clays are not many, and, as a rule, burners must recognize distinct stages of firing. Potters, as a rule, have not learned these lessons, and if the Veritas Firing Rings have no other value, it would be eminently worth every potter's while to study into this system, secure the apparatus and discs, and be coached in the proper method of burning his ware. For the potter must recognize distinct stages in the development of his ware in somewhat the same way as has the brick manufacturer.

DISCUSSION

Mr. Purdy: There seems to be no controversy of fact. It seems very strange, that anyone could warp my previous statements to infer that these rings were made of the Cook Pottery body. I knew they were not. My remarks were made to em-

phasize the fact, that these rings were made of the same materials as are in the Cook Pottery body, and hence should give results concordant with the physical changes in pottery wares. My remarks would not have been made, had not Mr. Watts stated that they contained something special, not ordinarily used in pottery body. In answer to direct question, he said, this special ingredient was magnesium oxide as was shown by analysis.

Mr. Watts: I do not remember saying, nor was there any evidence in the discussion of my saying that I knew positively they contained magnesium oxide; I think the speaker was confused. I did not know positively that they contained magnesium oxide. I was told, they were not made from the body of the Cook Pottery Company, which was the statement or rather the impression that one might naturally gain from the wording of your statement. I think if you will read that discussion over carefully, you will find that your statement was so made, that it was generally understood that you either positively stated that they were made of the Cook Pottery Co. body or at least you so expressed it, that, that was the impression taken. Now I have been told, and by individual statements made to me, I have been confirmed, that the composition of the rings, while it may have, to a certain extent, the same chemical composition as an ordinary pottery body, does not have exactly the same physical behavior as a pottery body. The physical behavior is more exaggerated in most instances than a pottery body would be; not that the relation of the fluxes is materially different, but we very well know that two clays may have the same chemical composition and yet, not be identical as regards physical properties, and it is the physical properties that are brought out in the Veritas Disc not the chemical properties. The physical property is the property that the Veritas disc depends on, for its value as a pyrometer, not the chemical property at all. I don't see that anything is gained by chemical analysis. You yourself have repeatedly said that you cannot tell anything about the behavior of a clay by its chemical analysis.

Mr. Purdy: Have you ever used the Veritas Rings?

Mr. Watts: Yes, at the Ohio State University, I have quite a stock that we have been testing.

Mr. Forester: I have not the slightest doubt but what Professor Purdy's feelings towards me are of the very best, but, when he stated, last year, at Wheeling, that the Veritas Ring is made of the Cook Pottery body, he was a long way off the mark. Now, I don't suppose for a moment, that you desire me to tell you exactly what I make my ring of, because, that would be rather a pertinent question, don't you think so? I am of the opinion that I could be of very great use to Professor Purdy, in the manufacture of his goods if he would permit me. Now may I suggest this to you, that this controversy be left over until your next meeting, and then, if you will allow me to explain the whole working of the Veritas Firing System, I shall be very pleased to do so. It is not in any way a theoretical question. The results of this firing system have been arrived at, by practical experience. I should have regretted very much, had the accident to my arm prevented my coming here, to hear the remarks on the Veritas Firing System, and, to make your acquaintance. I have heard a great deal discussed here, wherein I think I might be useful to some of you, by giving you my experience as a potter in England during the last thirty-three years. It seems to me, that whatever class of pottery you may be manufacturing you should adopt a system of firing, that will enable you to standardize your goods, and obtain a true percentage of the result of each kiln. I contend that the Veritas Firing System will enable you to do this. It is not a difficult matter to systemize your firing. The size of your kiln, and the thickness of your pottery will give you the time you should fire, and your body mix will give you the heat to which you should go.

With your permission, on a future occasion, when I hope to be in a better condition for talking, I shall be very glad indeed to go into this important matter, and, to answer any questions you may desire to put to me.

THE EFFECT OF LIME ON CERTAIN CRACKING CLAYS

BY N. B. DAVIS

In many parts of the United States and of Canada occur clays and shales from which it has been impossible to make clay ware because of cracking in air drying. In the Canadian northwest, clays of this type are particularly abundant, and, in some districts no other clays of workable character are present. To remedy this, the Canadian government and private individuals have spent much time and money, investigating means of overcoming this difficulty.

In 1911 Orton[1] published the results of his experiments along this line on clays from the Edmonton district. Various chemical coagulants were used such as HCl, NaCl, etc., but in each case these were reported ineffective or impractical. The method finally adopted was that advanced by Bleininger[2] of preheating the clay to a temperature at which part of the structure was destroyed, which treatment was sufficient to make the material workable.

Preheating the clay, however, is too costly to allow of its use except under very favorable conditions as regards fuel supply, a condition which prevails to some extent at Estevan, Saskatchewan.

These methods have been tried out on Canadian clays by Ries and Keele and their results are to be found in the *Memoirs of the Canadian Geological Survey.*[3]

So far then, there has been developed no really cheap, practical way in which these cracking clays could be made use of, for burned clay products, excepting for railroad ballast.

The Agricultural Use of Lime. Let us now consider a practice long in use in agriculture for fertilizing and granulating soils. For many years it has been the custom on the farm

[1] Orton, *Trans. Amer. Cer. Soc.*, Vol. XIII, 1911.
[2] Bleininger, *Trans. Amer. Cer. Soc.*, Vol. XI, 1909, p. 392.
[3] *Memoirs*, 24 E., 25, 37, 39. Can. Geol. Survey.

to add to the soil, lime in the form of burnt lime, hydrated lime, ground limestone, or marl. It is generally known that ground limestone or marl helps in time to granulate the soil, but writers on the subject call special attention to the value of either burnt or hydrated lime as a means of quickly granulating a heavy sticky soil. So important is the effect of a generous supply of lime in opening up the soil that the saying "a lime-rich soil is a fertile soil" has become common.

Russel[4] makes the following statement in this connection: "In general sandy soils require only sufficient (lime) to prevent sourness, while clay soils need in addition enough to keep the texture good. It commonly happens that 0.5 percent of calcium carbonate proves inefficient for clay soils, and even 1.0 percent may not be enough in highly farmed districts, especially where cattle are fed on the land and tread the soil into a somewhat sticky state."

By the addition of lime to clay soils the agriculturist has improved their working qualities. Why cannot the ceramist make use of the same phenomenon?

Last year, while working with excessively plastic clays in connection with a study of plasticity, the above described method of treating clay soils was noted and provision made for trying it out on clay at hand. However, that point was not reached, but during the summer the effect was demonstrated to the writer by Mr. Jas. Keele in his laboratory at Toronto University. Mr. Keele has completed a series of tests on western clays and is publishing the results in a forthcoming memoir of the Geological Survey of Canada.

On returning to Cornell this last fall, experiments were started on a number of clays, mixing them up with varying percentages of Kelly Island hydrated lime. After some work had been done, it was seen that two types of cracking clays could be distinguished. In the first place, there are those in which the gelatinous matter causing the excessive plasticity and shrinkage is of an inorganic nature; and in the second place, those in which the gelatinous matter is mostly of an organic character.

[4] *Soil Conditions and Plant Growth.*

Experiments. Four clays, representing as many degrees of cracking, were taken and trial pieces molded to a size two and a half inches square. One trial piece of each was made containing only the raw clay, and other trial pieces were made using varying percentages of the lime. Each clay was ground to pass

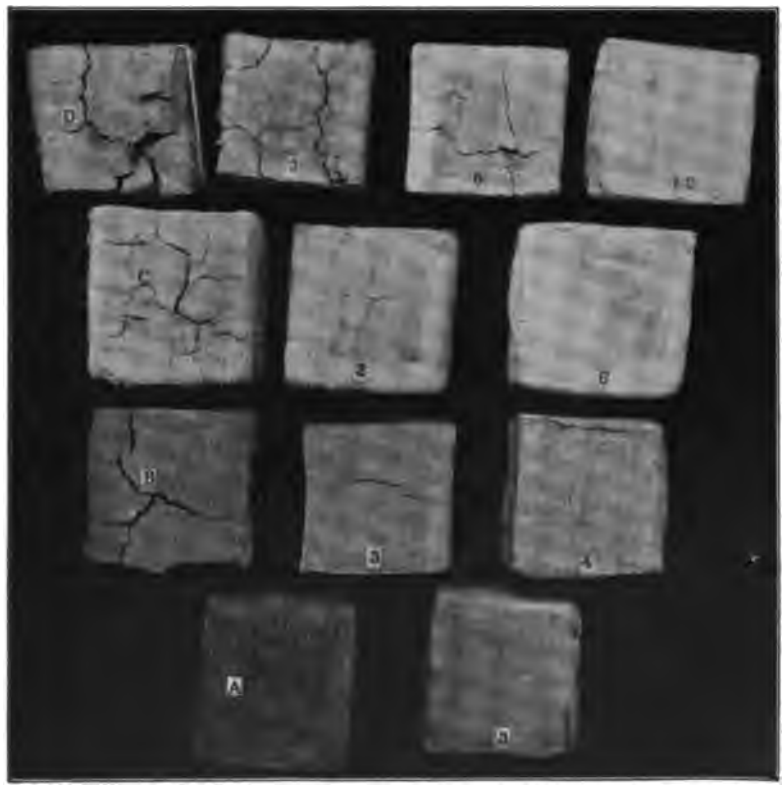


FIG. 1

CLAY	PERCENT LIME
A	0, 3,
B	0, 3, 4.
C	0, 3, 6.
D	0, 3, 6, 12.

15 mesh, and the lime mixed in dry. Water was added in the usual way and it was surprising to notice the sudden change in the working qua.ities or plasticity. Trials D and C were exceedingly sticky and hard to work in the untreated state. Trials A and B did not crack so very badly in the untreated state. But three percent of lime was required to stop the cracking in A, and but four percent in the case of B (Fig. 1). They are typical of many tender clays at present being used with difficulty for brick making in various parts of the country.

On the other hand, trials D and C represent clays that crack very badly in drying and are very sticky and hard to work. Trial C was high in inorganic gelatinous matter (hydrous silica and silicates) while sample D is low in hydrous silica and high in organic gelatinous matter. It was necessary to add six percent of lime to sample C to do away with the cracking, and at this stage sample D was still sticky. It was not until as much as twelve percent of lime had been added to D that the cracking was overcome. This was expected in this case, since lime seems to have little effect on organic matter until present in great excess.

Sample C represents a two-and-a-half foot bed of a white to cream burning shale found under a coal seam at Princeton, B. C. Test pieces of the untreated shale burned to a light porous body at cone 05, drying cracks being present however. With six percent lime the cracking was overcome, shrinkage was decreased slightly, and burning to cone 05 developed a good strong body, light weight and porous. This shale, if ground and treated with lime would make excellent partition block.

Some readers of this paper may perhaps question the advisability of adding lime to a clay, on account of its action as a flux, but evidence is at hand to show that clays of the type under consideration are nearly free of lime.

In clay pits in which the original clay was of a calcareous nature, it has been observed that as a rule the weathered top, leached of most of its lime is very much more plastic than the unleached part. Of course, it may be argued that simple leaching of the lime is not the only change but it is plain in the light

of the results obtained by the restoration of the lime, that lime is a controlling factor.

In the analyses of clays which crack in drying, it is interesting to note the low percentages of lime. The following analyses illustrate this:

TABLE I

	No. 1	No. 2	No. 3	No. 4
	percent	*percent*	*percent*	*percent*
SiO_2	74.25	65.23	69.14	55.0 to 65.0
Al_2O_3	14.29	18.60	14.50	15.0 to 20.0
Fe_2O_3	2.89	2.97	2.56	5.0 to 7.0
CaO	0.37	0.66	2.45	1.0 to 3.0
MgO	trace	0.64	1.14	0.5 to 2.0
K_2O	2.52	2.40	0.19	2.5 to 4.0
Na_2O	1.19	2.23	1.25	
Loss	4.21	7.30	7.71	6.0 to 10.0
CO_2	none	0.42	0.52	

(1), (2), (3), Memoir No. 25, *Can. Geol. Surv.*, p. 89.

(4), Range of a number of gumbos. *Clays of Missouri. Missouri Geol. Survey.*

Clays containing as much as thirteen to twenty percent of lime are reported by Ries[5] to be in common use for making common crick, common earthenware, roofing tile and some terra-cotta. He mentions one clay being worked in Texas as containing forty-one percent of lime. Hence the addition of six to twenty percent of lime would not be dangerous.

According to MacIntire[6] magnesia has a greater affinity than lime for the hydrous silicates and silica of clay, and by the use of a dolomitic lime (magnesia lime) the fluxing effect of the lime might be considerably modified. Barringer[7] has noted that magnesia introduced into a body increases shrinkage (fire), lowers the density and makes a "short" mixture to work. The most interesting experimental results reported by him were those of the "shortening" of the mixture, and that increase in shrinkage is opposed to the retarding of lime.

[5] *Clays, their Occurrence, Properties and Uses*, p. 93.
[6] Bull, No. 107. Tenn. Agr. Exp. Sta.
[7] Barringer, *Trans. Amer. Cer. Soc.*, Vol. VI, p. 90.

Of course the burned color would be influenced by the addition of lime, but in certain cases that would be of small importance when considering the need of a community for burned clay products.

Probable Cause of Physical Change on Addition of Lime. The soil chemists have done much work on the effect of lime on soils, and it is to them that we may look for a partial explanation.

The soils of the agronomist are often the clays of the ceramist. Although both are studying their materials toward different ends, yet they have much in common in the study of the physical and chemical nature of their materials.

Clays are the most complex mixtures with which the investigator has to deal. They are so complex and more often so finely divided that as yet we have not been able to devise means of separating their various constituents. However, we do know a certain amount about them. For many years the mineral kaolinite was considered the base of all clays, but today our knowledge has advanced far enough to contradict that.[8] It is only one of the many possible hydrated silicates developed by the weathering of more complex silicates. Besides these there may be present various silicic acids in such form as to be difficult or impossible of determination. Many of them are present in a very finely divided colloidal gelatinous form, and, when plentifully present, increase the plasticity to excess, and it is these substances that must be dealt with in cracking clays. They are acids and acid salts, and they will react with a strong base like lime to form a new chemical arrangement with different physical properties from those of the original.

The soil chemists have shown that silicic acid is readily attacked by caustic lime and more so by magnesia. A recent bulletin, (No. 107, of the Tennessee Agricultural Experimental Station, by MacIntire, Hardy and Willis) discusses these facts in some detail as applied to soils, although the time element is of so small importance to them in their work that the carbonates of lime and magnesia were used. MacIntire, Hardy and Willis

[8] This was probably first suggested by G. P. Merrill.

found CO_2 to be evolved from the contact of calcium carbonate or magnesium carbonate with silicates and pure silica under moist conditions; and that this action increases with the fineness of division of the reacting substances. The evolution of CO_2 indicates a chemical change taking place.

It is generally believed that the hardening of mortar is in part due to the formation of calcium silicate; and the superiority of the mortar in the structures built by the Romans has been attributed to the mixing of sand with newly hydrated lime as contrasted with present day methods.

In the cracking clays, the substance causing the trouble is the very finely divided matter which has a great affinity for water. Lime also has a great affinity for water as is well known. By getting an intimate mixture of clay and lime in the dry state and then adding water, chemical reactions take place between the lime water and clay matter, and conditions are favorable to the immediate formation of lime salts with the acid silicates and silicic acids.

The soil chemist states that caustic lime is an active destructive agent of organic material when applied in proportions of ten percent or larger. This was apparent in the case of sample A to which it was necessary to add twelve percent of lime to destroy the effect of the organic gelatinous matter and stop the cracking.

The Use of Lime in Practice. It would be impossible to get lime into an intimate mixture with the clay particles by adding it with the tempering water. The lime must be added to the clay in the dry powdery condition and the two thoroughly mixed before any water is added. In practice this would require the clay to be brought to the machine in a dry condition. It would then have to be ground to 15 mesh, and the lime thoroughly incorporated in a suitable mixer before passing on to the tempering pug. Beyond this stage the treatment in the brick making would be subject to the usual variations.

The cost of the lime treatment would depend on the location of the clay with regard to the lime supply. This lime cost might

be cut down by the use of a certain amount of grog, but the amount suitable would need to be determined in the field.

In conclusion it may be stated that the use of lime to stop cracking seems perfectly feasible so far as laboratory experiments go. It requires to be tested out on a factory scale.

DISCUSSION WRITTEN AFTER READING THE PAPER

Prof. Staley: As I understand this paper, the use of lime is proposed as a practical method of overcoming cracking, only in such cases where the preheating treatment cannot be employed on account of the high cost of fuel. Considering the differences in burning properties and quality of ware that would be produced by the two methods, the cost of fuel for preheating purposes would have to be inordinate before the treatment with lime would be a serious competitor. In this connection, it must be remembered that the cost of adding three to twelve percent of lime would be no small item of expense to a plant making only inferior ware. It is assumed, however, that Mr. Davis knows his territory and has made calculations of the comparative cost of the two methods. As far as the United States is concerned, on the basis of cost and value of product, the preheating treatment would probably have the preference in every instance.

In cases where the preheating treatment cannot be employed, either on account of cost or, more probably, because it is not effective, it would seem that the use of common salt should be seriously considered. While salt is more expensive than lime, the amounts required are not as great, and it does not cause the deterioration in value of the product that the lime treatment does. The work of Ries and Keele has shown that comparatively small additions of salt made a marked improvement in the drying properties of many Canadian clays. This method has been used for years in the drying of Tertiary clays at certain plants in the northwestern part of the United States. Since the bar to the use of preheating treatment in many cases is that the plasticity and working properties must be destroyed before the clays will dry safely, it might be possible to combine a mild preheating treatment with subsequent treatment with small additions of either lime or common salt.

DATE
AUTHOR
SUBJECT
FORM 40

NG OF GLASS

AND PAUL D. NECKERMAN

e savage, and probably even civ-
. the image reflected by the quiet
tory of attempts to picture him-
'entateuch tells of brass mirrors
Egyptians, Greeks and Romans
)ecimens of which are preserved
mirrors were usually disks of
on one side and bearing a design
netal was also employed, and the
m silver and gold.

'y, XXXVI, 66, p. 193, mentions
of glass mirrors at Sidon. Evi-
ers, would indicate that the older
)ns into which molten lead or al-
were subsequently cut into discs
. globes of glass were filled, while
and antimony with tar or resin.
The filled globes were then cut into lenses known as *"Ochsen Augen,"* bulls' eyes. This process was in use before the sixteenth century.

In 1507, an exclusive monopoly for twenty years was granted two inhabitants of Murano who claimed to possess the secret for making perfect mirrors. Practically all mirrors previously referred to were small, *i. e.,* hand mirrors. The Venetian mirrors were made from cylinders of glass which were slit and flattened, carefully polished, and the edges frequently beveled. The backs were silvered by an amalgam probably of tin. One of these mirrors 46 by 26 inches, listed with other effects of the French minister Colbert, was valued at 8016 livres (1 livre=19½ cents) while a Raphael painting was appraised at 3000 livres. Through Colbert's efforts, Venetian workmen were brought to France in 1665, and these, together with Richard Lucas, who had

been practicing the art in France since 1653, carried the art to a high state of perfection. A further impulse came in 1691 with the introduction of plate glass manufacture. In the old method, the polished plate was lowered, by gradual inclination, onto a bed containing a rather liquid tin amalgam. Weights were then placed on the glass to squeeze out excess mercury, and the table was inclined to allow this to run off. The hard amalgamated foil would then adhere to the glass.

In 1836, Justus Freiherr von Liebig made the first attempt to back glass with a silver film deposited from aqueous solution. In the Liebig method, an alkali was added to the silver solution which was then precipitated by aldehyde. The mirrors became spotted after a time, so the method was apparently abandoned. The authors have found that when formaldehyde is added to an ammoniacal silver solution very promising results are obtained. These will be discussed later. Some old letters of Liebig's are being published serially in the *Zeitschrift fur Angewandte Chemie*. Those which have appeared to date, (May, 1915), contain nothing new on the silvering question.

Petitjean patented a process in 1855 which is, with slight modifications, the one in use today. It consists of solution **A**, 1 oz. silver nitrate dissolved in 2 oz. distilled water with addition of ammonium hydroxide until the brown precipitate is nearly redissolved. The solution is filtered and diluted with distilled water to 6 oz. Solution **B**, 35 g. tartaric acid in 6 oz. distilled water. The latter is the reducing solution. At St. Gobain two reductions are made, the quantity of tartaric acid being doubled for the second bath.

For the benefit of those unfamiliar with the process of silvering plate, it might be said that after the elimination of imperfect parts, the sheet is cut into desired sizes, beveled and thoroughly cleansed, finally being rinsed in distilled water. It is then placed on a warming table, and the silvering solutions are poured onto the plate. Heat helps or hastens the mirror formation. After silvering, the plate is again washed, then dried, coated with shellac and painted.

Palmieri's Process. **A**, silver nitrate 1 oz., water 10 oz. **B**, potassium hydroxide 1 oz., water 10 oz. **C**, glucose ½ oz., water 10 oz. Add ammonium hydroxide to **A** until turbidity first produced disappears; then add **B** and again ammonium hydroxide until clear; then more silver nitrate until cloudy; finally **C** and apply to clean glass surface at 56°F. Film said to form in 43 minutes.

Barton's Process. **A**, silver nitrate 25 gr., water 1 oz. **B**, potassium hydroxide 25 gr., water 1 oz. **C**, 1 part **A** and 1 part **B** with ammonium hydroxide to disappearance of precipitate and enough of **A** to just bring it back. **D**, loaf sugar 2700 gr., water 20 oz., nitric acid 2 drops, alcohol 10 oz., water to make 80 oz. For use: Solution **C**, 1 oz. with solution **D**, 1 drachm.

Draper's Method. **A**, sodium potassium tartrate 500 gr. in 3 oz. water. **B**, silver nitrate 800 gr. in 3 oz. water. Add **B** to 1 oz. ammonium hydroxide until permanent brown precipitate forms and then ammonium hydroxide and silver nitrate solution alternately until the latter is exhausted. A little of the brown precipitate should remain. Filter. Just before using mix solution **A** and dilute to 22 oz.

Martin's Method. **A**, silver nitrate 175 gr. in 10 oz. water. **B**, ammonium nitrate 262 gr. in 10 oz. water. **C**, potassium hydroxide 1 oz. in 10 oz. water. **D**, pure sugar candy ½ oz. in 5 oz. water. After solution add 50 gr. tartaric acid, boil 10 minutes cool, add 1 oz. alcohol and make up to 10 oz. with water. For use take equal parts **A** and **B**, mix, and add mixture of equal parts **C** and **D**. Mix both mixtures in the silvering vessel and suspend glass object to be silvered, face down in the solution.

Brashear's Process. Reducing solution: Loaf sugar, 90 grams, nitric acid (sp. gr. 1.22) 4 cc., alcohol 175 cc., water 1000 cc. Use quantities indicated in Table I.

Many other formulas appear in the literature, but as most of them are published anonymously, they have not been included here. The Brashear process is apparently the only one which shows a tendency to approach the subject quantitatively.

TABLE I

MIRROR DIAMETER	AREA	$AgNO_3$	KOH	$NH_4OH + H_2O$	REDUCING SOLUTION
cm.	*sq. cm.*	*grams*	*grams*	*cc.*	*cc.*
30	757	15	7.5	12	85
25	491	11	5.5	9	65
20	314	7	3.5	6	40
15	177	4	2.0	3	25
10	78.5	1.8	0.9	1½	10
5	19.6	0.5	0.25	1½	3

Purpose of the Authors' Investigation. The authors propose to conduct a thorough and systematic qualitative and quantitative study of methods for the precipitation of metals in mirror form from solutions of their salts. The necessity for this is already apparent from a study of processes cited, possibly excepting the last one given. One large manufacturer is using honey and alcohol to reduce his silver. Many manufacturers are wasting large quantities of silver through inefficient methods, so there is further need for the study of this subject as a matter of economy.

This paper contains the qualitative results and bibliographical material obtained to date. Subsequent installments will give the quantitative data. In following experiments, a fifth molecular silver nitrate solution, precipitated by ammonium hydroxide and precipitate practically redissolved, was employed. As to the other data, Table II is self explanatory.

TABLE II

NOS.	REDUCING AGENT	TEMPERATURE	CONCENTRATION	RESULTS IN 6 BY ⅝ INCH TEST TUBES
1	Sodium and potassium tartrate	hot	concentrated	Film formed immediately. Solution first turning brown and finally black. Good mirror.
2	Sodium and potassium tartrate	cold	concentrated	Film formed in thirty minutes; complete in forty-five minutes. Solution darkened finally turning black. Good mirror.
3	Sodium and potassium tartrate	hot	dilute	Film formed in ten seconds. Solution first turning brown and finally black. Good mirror.
4	Sodium and potassium tartrate	hot	dilute	Small quantity of silvering and reducing solution placed in tube, mixture heated and tube shaken till the film was complete. Film formed quickly, solution first turning brown and finally black. Fair mirror.
5	Formaldehyde	hot	2cc. 40 percent formaldehyde	Acted quickly. Bubbles of gas given off. Mixture quickly turned dark brown. Slight silver film formed in spots. Poor mirror.
6	Formaldehyde	cold	2cc. 40 percent formaldehyde	Action fairly rapid. After shaking solution changed color, first darkening, then assuming a violet color, and finally black. Good mirror. Mirror not formed as quickly as with sod. and pot. tartrate. Mirror with sod. and pot. tartrate and reducing sugar formed quickly. With formaldehyde, silver film is built up gradually.

TABLE II—Continued

NOS.	REDUCING AGENT	TEMPERATURE	CONCENTRATION	RESULTS IN 6 BY 5/8 INCH TEST TUBES
7	Formaldehyde	cold	2cc. 40 percent formaldehyde	Action fairly rapid. Solution assuming violet hue. Solution removed before mirror was completely formed. This film shows that silver builds up gradually.
8	Formaldehyde	cold	dilute — few drops used	Action fairly rapid. After shaking, solution changed to violet, finally black. Good mirror.
9	Tartaric acid	hot	concentrated	White precipitate, turning brown. Film in ten seconds. Good mirror.
10	Tartaric acid	cold	concentrated	White precipitate. No mirror, even on long standing.
11	Tartaric acid	hot	dilute	Slight white precipitate, quickly turning blackish gray. Silver in film formed rapidly. Fair mirror.
12	Citric acid	hot	concentrated	White precipitate. No mirror, even on continued heating.
13	Citric acid	cold	concentrated	White precipitate. No mirror.
14	Citric acid	hot	dilute	White precipitate. No mirror.
15	Citric acid	cold	dilute	White precipitate. No mirror.
16	Dextrin	hot	concentrated	Solution turned brown and finally black. Thin dark film. Poor mirror.
17	Dextrin	cold	concentrated	Solution darkened slowly. No mirror.

18	Dextrin	cold	dilute	Solution darkened slowly. No mirror.
19	Dextrin	hot	dilute	Solution turned dark brown. No mirror.
20	Tannic acid	hot	concentrated	Black precipitate. No mirror.
21	Tannic acid	cold	concentrated	Black precipitate. No mirror.
22	Tannic acid	hot	dilute	Black precipitate. No mirror.
23	Tannic acid	cold	dilute	Black precipitate. No mirror.
24	Sodium tartrate	hot	dilute	Film formed in ten seconds. Action same as tartaric acid. Good mirror.
25	Sodium tartrate	cold	dilute	Film formed slowly, complete in fifteen minutes. Poor mirror.
26	Milk sugar	hot	concentrated	Film formed in three minutes. Very dark mirror.
27	Milk sugar	hot	dilute	Film formed in five minutes. Good mirror.
28	Milk sugar	cold	concentrated	No effect.
29	Milk sugar	cold	dilute	No effect.
30	Stannous chloride	hot	dilute	Dark gray precipitate. No mirror.
31	Stannous chloride	cold	dilute	Dark gray precipitate. No mirror.
32	Cane sugar (inverted with HNO_3)	hot	concentrated	Solution turned dark red brown, finally black. Film formed within ten seconds. Good mirror.
33	Cane sugar (inverted with HNO_3)	cold	concentrated	Solution turned dark red brown, finally black. Film formed slowly, complete in thirty minutes. Poor mirror.

TABLE II—Continued

NOS.	REDUCING AGENT	TEMPERATURE	CONCENTRATION	RESULTS IN 6 BY 5/8 INCH TEST TUBES
34	Cane sugar (inverted with HNO_3)	hot	dilute	Solution turned dark red brown, finally black. Film formed within ten seconds. Good mirror.
35	Cane sugar (inverted with HNO_3)	cold	dilute	Solution slowly turned dark red brown, finally black. Film formed slowly and was complete in thirty minutes. Good mirror.
36	Phenylhydrazine	hot	dilute	Solution rapidly turned black. Bubbles of gas given off. Pieces of tarry substance choked the tube. No mirror. Slight black coloration on side of tube.
37	Phenylhydrazine	cold	dilute	Solution rapidly turned black. Bubbles of gas given off. No mirror.
38	Formic acid	hot	dilute	No effect.
39	Formic acid	cold	dilute	No effect.
40	Formic acid	cold	concentrated	No effect.
41	Formic acid	hot	concentrated	No effect.
42	Potassium nitrite	hot	concentrated	Slight precipitate. No mirror.
43	Potassium nitrite	hot	dilute	Slight precipitate. No mirror.
44	Potassium nitrite	cold	concentrated	Slight precipitate. No mirror.
45	Potassium nitrite	cold	dilute	Slight precipitate. No mirror.

46	Sodium sulphite	hot	concentrated	No effect.
47	Sodium sulphite	hot	dilute	No effect.
48	Sodium sulphite	cold	concentrated	No effect.
49	Sodium sulphite	cold	dilute	No effect.
50	Nitrous acid	hot	dilute	No effect.
51	Nitrous acid	cold	concentrated	No effect.
52	Nitrous acid	hot	dilute	No effect.
53	Nitrous acid	cold	concentrated	No effect.
54	Ferrous sulphate	cold	dilute	Black precipitate. Slight black coloration in spots. No mirror.
55	Ferrous sulphate	hot	dilute	Black precipitate. Slight black coloration in spots. No mirror.
56	Acetaldehyde	cold	dilute	Act on same as formaldehyde. Good mirror.
57	Acetaldehyde	cold	dilute (more dilute than above)	Act on same as formaldehyde. Good mirror.

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Department of Chemistry,
University of Pittsburgh

DISCUSSION

Mr. Frink: Speaking about efficiency, I know of a plant where they make mirrors for automobiles; it started in with rather a high efficiency as to what they did. They purchased 587 oz. of silver in one week and returned 604 oz. of chloride—that is the efficiency they got. They were handicapped, however, because they had to have a vessel in which to suspend the mirror, and there was a little instance there, that would be worth repeating. The place where they made these mirrors was over the grinding room of the establishment, and the vibration which was caused by the machinery gave them an effect upon the tenacity, the completeness of mirrorizing, which I haven't found in any other establishment, so that the operation may be beneficial.

Prof. Silverman: I want to mention a fact which is exceedingly important and which was brought out in Mr. Frink's paper. Seeds are quite a factor in the silvering of plate mirrors, and in the polishing. If one of the seeds happens to crack, the cleaning solution often stays in the minute opening, and a spot results on the mirror. You will find by looking over the test tubes, that there are a few seeds which happened to burst on the inner surface, and the cleaning solution remaining there, spotted the mirror.

Mr. Frink: I would like to ask if Mr. Silverman would like to have some specimens of glass in which there are three or four or five seeds, to experiment on in his work?

Prof. Silverman: That might be interesting, but we want to make perfect mirrors.

NOTE ON PROS AND CONS OF USE OF ZINC OXIDE IN GLAZES FOR SEMI AND VITRIFIED CHINA BODIES

BY ROSS C. PURDY

In a note on "Comparison between English and American Clay Practice," Mr. Ernest Mayer, on page 309 of Vol. XVI of these Transactions, makes the statement that he cannot tell why zinc is used in the American earthenware glazes, and has never found anyone who could tell him. The writer feels sure that he has emphasized the pros and cons of the use of zinc oxide in these glazes on several occasions, but will repeat them here.

1st. **Why Zinc Oxide is Used.** It improves color; gives more gloss; gets away from the egg shell finish, helps to correct, or obviate crazing; gives longer heat range to the glaze, and is of great assistance in obtaining more easy fusibility, thus obviating the use of a large quantity of lead and boric acid.

The high surface tension of the surface of the glaze resulting from the use of zinc adds to the gloss. The decrease in lead results in a better white, and, in itself, adds whiteness to the glaze, and in many other respects is very beneficial to the glaze.

2nd. **Why Zinc is Not Used.** So far as the writer has been able to learn, there are only two real objection to the use of zinc oxide in these glazes. The first one is the effect on over-glaze and under-glaze colors. The use of zinc oxide in a glaze materially lessens the range of colors that are possible. Some of the most desired colors in both over-glazed and under-glazed would be destroyed by the zinc.

The second objection to the use of zinc oxide in china glazes, and this refers more particularly to the porcelain wares which are used in hotels and restaurants is the solubility of the zinc oxide in the caustic washing solutions used in cleaning the dishes. The writer knows, by actual observations, that the glazes containing zinc oxide are more easily destroyed by these solutions than are the glazes free from zinc oxide. Glazes containing zinc

oxide will soon become so pitted and roughened, that the silver plated knives and forks will leave a black streak upon them, and they will soon become dingy from use. If I were purchasing for a restaurant or hotel, I would insist that the glaze should be free from zinc.

A few of the restaurant and hotel keepers, with whom I have conversed on this point, have stated that from their experience, the egg shell finish denotes a hard glaze, one which will not be roughened by their washing solutions, and, hence, will not take the silver streaks and become dirty-looking through use. They, of course, have not known the composition of the glaze, hence attributed it altogether to hardness. I have found out, however, that the egg shell finish, generally, but not always, denotes freedom from oxide of zinc. The glazes in which oxide of zinc is present are more glassy and glossy. By experience and custom, therefore, restaurant and hotel keepers have learnd to choose the egg shell finish. In turn, the potter has studied how to produce this finish. If the trade demands this finish, then the potter had best not use zinc in his glaze.

It is not absolutely necessary to use zinc oxide in order to make a glaze that will be free from crazing. Body composition and biscuit firing are such strong factors in the control of crazing, that it is rather easy to overcome the advantages of zinc oxide in this respect. It is not so easy, however, to produce a pure white glaze without zinc oxide, nor to produce a glaze with the long heat range required by some pottery practices unless zinc is used. For the cheaper wares, the writer would advise the use of zinc. For the vitrified goods such as used in hotels and restaurants, and in wares where a large selection of colors is desired, it would be best not to use zinc oxide.

There is no argument at all regarding the volatilization of zinc oxide for very little if any trouble results from this.

DISCUSSION

Mr. Mayer: The question of the use of oxide of zinc has often been mentioned, and I think that what Mr. Purdy said is probably true, that is, I have never used the glaze myself which contained oxide of zinc. I mean to say, I have never used it on

my own wares. I have been called upon many times to provide certain colors for the use of manufacturers. We used glazes that have got zinc in them. The colors that I produced and was making could not be duplicated underneath those glazes. I have many times asked potters, my friends and well posted men, too, why oxide of zinc was used, and I got as many different answers to that, as I asked questions, I think. Some people told me it was used in the glaze to make the glaze slightly opaque. Now, I don't think it has that effect, because the trade marks underneath the glaze were always sharp and clear, and the glaze did not show any sign of opacity. The use of oxide of zinc in a glaze certainly allows less lead to be used, there isn't any question about that, and any lead that is cut out of a glaze certainly helps the color of the glaze, and there is no question about that. I believe that that is the reason why the zinc is used in the glaze, on account of its having a tendency to make a better color of the glaze, because of the less amount of lead that is used. That is a very good reason too, I think. The use of zinc in a glaze is peculiarly an American practice. I have seen many thousands of mixtures of glazes, I believe, of European origin, and I fail to find, that it has ever been mentioned in any European glaze I have seen; and for that reason, possibly, it is rather a poor argument to use, I admit, but for that reason, I supposed that there was nothing particular to be gained in the use of it, or it would be used by the European manufacturers. But as far as the advantages have been brought out by Prof. Purdy, I think the great one, after all, is that it improves the color of the glaze on account of less lead being used. That is certainly something in its favor. So far as its use for general underglaze work is concerned, I state distinctly that I never used it myself and only experimented on those glazes that have been used by others, consequently I haven't very much right to say much on that subject. The use of oxide of zinc, Prof. Purdy says, makes a very much more glassy appearance to the glaze. That, I would say, is decidedly objectionable. Possibly not so, as he said, with some people, but as a rule,, we don't want to get that effect, we want to get more the effect that is produced by the hard porce-

lain glazes; that, I think, is probably the standard. Now I have never objected in any way to the use of oxide of zinc. As far as I am concerned, I never used it myself, but I think it has certain advantages, and those have been very clearly brought out. If the advantages that have been brought out overbalance the disadvantages, it is certainly proper practice for those people to continue to use it that have done so, but I would much prefer to go on as I have without the use of it.

Mr. Jackson: Mr. Purdy makes the statement that a glaze containing zinc was harder than a glaze that did not contain zinc. I take it that Mr. Purdy means by this that a glaze containing zinc is harder from the standpoint of abrasion. It has been my experience that a glaze formula of a trisilicate ratio is more resistant to abrasion and will mature at a slightly lower temperature than the same glaze without zinc. This question is one that is of vital importance to the china manufacturer, a large proportion of his product is used in the hotel and restaurant business. The conditions of service are far different than that met with in the home. In the first place, the hotel uses a mechanical dish-washing machine, in some instances the action is wholly abrasive, the pieces of china in the container wearing one against the other at the same time being submerged in hot water which has been made strongly alkaline to cut the grease. In the main, the ware is transferred from the strong alkaline solution to one of clear hot water in order to wash off the alkaline solution, and very often, the rinsing water becomes alkaline, and the ware goes to the drying oven to be dried covered with an alkaline solution. The old method of drying dishes with a dish towel is obsolete in the modern hotel kitchen; the ware is usually so hot after it comes from the washer as to need but racks on which to place them. After the evaporation has taken place, there is left on the piece of china a thin film of alkali, and in the drying oven this bakes onto the ware very hard. Successive films are deposited with the result, that a glaze is called unsatisfactory, when, in fact, the glaze is in no way responsible for the condition. A dilute solution of acid will sometimes place the blame where it belongs. The dish washing machine, and the new con-

ditions it has created, have given the china manufacturer problems for consideration that are entirely due to the advent of this machine.

Since the question after all, is largely one of resistance to abrasion, we conducted an extended series of experiments to find out which of the glaze making materials tended to increase or decrease this resistance. The resistance is measured by the loss in weight after each test. The method consisted of firing each glaze in a three inch baker after this had been filled with dry powdered glaze. This gave us a receptacle that was about two-thirds full of melted glaze, and we then forced this against a carborundum wheel for a given period of time, aiming to duplicate conditions on each separate test. The results on a duplicate set indicated that the procedure gave a relative value.

The whole series of tests can be summarized as follows: "The resistance of a glaze to abrasion is proportional to the perfectness of its fusion." An increase of the fluxing elements in each test increased the resistance to abrasion. The following fluxes giving the greater resistance: borax, zinc, calcium fluoride. The above tests were made for the purpose of indicating the path to be followed. Aiming to incorporate the facts enumerated above, glazes were made up and tested in a sexagon machine, in which six plates could be fastened, then mechanically rotated, the mill contained twenty-five pounds of bitstone (granulated quartz rock) and rotated for 24 hours. Here again the results are purely relative, as the test is a comparative one.

The later work corroborated the facts brought out in the beginning, viz., that the resistance to abrasion of a lead silicate is proportional to the perfectness of its fusion, rather than to its chemical composition, however, since the two facts are so interrelated, it is difficult to be specific.

It has been contended by many, that those glazes lowest in fluxes and highest in alumina and silica were harder than those high in fluxes and low in alumina and silica. They are harder in the sense of taking increased temperature to mature them, but in this sense only. From the standpoint of resistance to abrasion, they are not.

Mr. Stover: As Mr. Mayer has said, you do not find any of the European glazes that contained zinc. I think I found the explanation of that in some of the works on glass. The glass data is pretty carefully worked out and gives comparisons on tenacity which would be exactly the value you would obtain from zinc, *viz.* 0.15, while lead would be 0.025. So you see, that zinc would be many times harder as regards hanging fast, than lead would be. That would be in glass mixtures, and of course a glaze is similar to a glass. Knowing some people who use zinc in their glaze, I tried to find out some reasons why. Of course, it produces opacity, if present in large quantity.

Mr. Purdy: The question of the consumer is, will a glaze retain its original resistance to wear and silver marking after having been washed in the alkaline solutions not three times a day but a dozen times during each meal. A plate used in a hotel probably is washed ten to twelve times during each meal. And the solution in which they wash these plates is very strongly caustic. It is really surprising how strong they make these solutions, because they have got to cut that grease off, rinse them in hot water and allow the plates to dry quickly from the heat of the hot rinsing water. They have to shuffle those plates very rapidly. That solution has got to cut that grease absolutely sure, so that when the plate comes to you it is spotless. You have noticed the waiter wiping off a plate—he is wiping off a little spot that did not dry bright. That solution is going to attack the zinc in the glaze. Will the glaze, after having such service, be as resistant to abrasion as it was before?

Mr. Stover: I would like to say yes; a great deal of ware that was made by Mr. Mellor's father, who has long since gone the "big voyage," is still without any crazing. I was looking for an explanation, and I find that one of the explanations as to why that was true is, that zinc oxide had a comparatively low co-efficient of contraction and expansion.

Mr. Purdy: Was that observation made of ware on the shelf or in home use?

Mr. Stover: It was on ware in use in the house, but I was not at that time considering zinc oxide, I was talking lead craz-

ing at that time, while, now, I am talking about the use of zinc oxide in reducing crazing.

Prof. Staley: Prof. Purdy's remarks as to disintegration of the glaze due to the effect of chemicals seems rather contrary to the findings of people who have made a careful study of the effect of the ingredients of glasses under the action of chemicals. Practically all chemical glassware which is used and which is designed especially to resist the action of chemicals, both alkaline and acid, contains zinc. The most resistant glass found in all the researches carried on at the Jena Glass Factory was quite high in zinc; and all the high grade chemical glass wares now in use contain a large percentage of zinc oxide.

Mr. Silverman: I would like to supplement Prof. Staley's remarks by calling attention to the fact that there were also considerable quantities of aluminium present in these glasses; and where you have three or four percent of aluminate present, it retards devitrification. The introduction of a little aluminium will permit of the addition of considerable quantities of lime, where otherwise the glass would be devitrified on account of the large amount of lime present, so I don't know that we can attribute that property of Jena glass to the zinc oxide alone.

Prof. Staley: In the experiments to which I referred, they made systematic investigations and varied the R O, only retaining the zinc content, and keeping the alumina and silica the same, and found that the zinc oxide as an R O element had a decided effect on increasing the resistance of the glaze to chemical action.

Mr. Silverman: Then the resistance is not entirely due to zinc oxide?

Prof. Staley: Surely not.

Mr. Silverman: But is modified by the addition of zinc to an already resistant glaze. The ZnO alone is not responsible for the resistance to chemical action, and devitrification would set in if it were not for the R_2O_3. The crazing tendency would prevent its use in china if it were not for the R_2O_3 present.

PROGRESS IN ECONOMY AND EFFICIENCY IN FIRING

THE DRESSLER TUNNEL OVEN

BY P. D'H. DRESSLER AND B. A. CANTAB, LONDON, ENGLAND

There is no doubt that in pottery, the branch of the manufacture which has advanced least is that of firing. In many factories, the up-draught kiln perfected by Wedgewood in the 18th century is still in use. It is the expense and the uncertainty of the firing operation which has, so far, prevented the industry from striding forward.

The object of this article is briefly, to show how it is that the older methods of firing are costly and inefficient, what attempts have been made towards progress and finally, how the Dressler Tunnel Oven, which has now been working successfully for three years, has overcome these difficulties and reduced firing to a simple, certain, and economical process.

It is fairly easy to calculate the actual proportion of fuel required to fire up pottery. For the sake of simplicity, let us consider the case of glost firing at 1070°C., using a fuel of calorific value 7500.

The specific heat of burnt clay is approximately .25, therefore to heat one gram of this material, let us suppose from 20° to 1070°, $.25 \times 1050 = 262.5$ calories are needed. One gram of the fuel on burning gives rise to 7500 calories, therefore, the proportion of fuel required is

$$\frac{262.5 \times 100}{7500} = 3.5 \text{ percent}$$

of the weight of the goods, supposing that the fuel gives up all its heat of combustion to the goods (which is of course not possible in any oven, the least of all in intermittent ovens). This is a very different figure from that obtained in actual practice.

The following figures have been placed at the disposal of the author, by the kindness of the manager of a well-known Stafford-

shire pottery, whose experience in various works in England and on the Continent lends them additional value.

They refer to a large up-draught kiln of no less than 8732 cubic feet capacity, and therefore as economical as it is possible for such a kiln to be. The temperature of firing is 1070°C. (cone 02a).

The details of the kiln are as follows:

Kiln size	8732 cu. ft.
Number of saggers	2361
Weight of saggers and goods	60.26 tons
Net weight of goods	13.17 tons
Average weight of sagger	44.7 pounds
Average weight of goods per sagger	12.5 pounds
Percentage of goods to total weight	21.8 percent
Fuel per kiln	16 tons
Percentage of fuel to goods and saggers	26 percent
Percentage of fuel to goods only	121 percent

In this case, the proportion of fuel to the actual goods is 121 percent, so that only $\frac{3.5}{121} = 2.9$ percent of the heat of combustion of the fuel is used in heating them up.

This wastage of 97 percent of the heat put into the oven can be accounted for by the following considerations:

1. The saggers, in which the goods are burnt, weigh nearly four times as much as the latter. All this weight, to be heated up to the same point as the goods, accounts for 10.4 percent of the fuel burnt.

2. When the oven is fired, the walls and the bottom of the oven must be heated up as well as its contents. In the case of the oven under consideration, the structure contains about 60,000 bricks weighing about 210 tons. The temperature of the inside is 1070°C., of the outside about 200°C. The average temperature of the brickwork is rather higher than the mean of these, owing to the fact, that the conductivity of fireclay is greater at elevated temperatures, thus there will probably be no very great error in assuming an average temperature of 700°C. for the oven walls.

In order to heat up fireclay to 700°C., we find in the same way as before that

$$\frac{.25\times700\times100}{7500}=2.33 \text{ percent}$$

of its weight of coal is required. For 210 tons, 4.89 tons of coal are needed, *i. e.* 30.6 percent of the fuel burnt. We see then, that more than twice as much heat is absorbed by the walls of the oven as by the goods and saggers.

3. When the oven is fired, it is evident, that the gases, which have traversed the oven and are escaping through the hovel, must be at least at the temperature of the goods they are leaving; thus all through the firing operation, there is an ever hotter stream of burnt gases escaping into the atmosphere. This is certainly the cause of a very important wastage of fuel.

4. In burning coal in the fireholes, it is a very difficult matter to regulate the supply of air so that there should only be just enough to burn the carbon to CO_2. In order to avoid reduction of the goods, it is necessary to fire with an excess of air. The additional cold air necessarily lowers the temperature of the flame. It will be seen from the accompanying table, how easy it is to reach a point at which the flame is no longer hot enough to raise the temperature of the goods, and when as a consequence the coal is being wasted.

Unit volume of air is that just required to burn the carbon.

VOL. OF AIR	THEORETICAL TEMP. OF FLAME
1	2821°
1.5	1874°
2	1381°
2.5	1126°
3	915°

The temperature given in the second column is that which would be obtained supposing the combustion of carbon to be carried out in a closed space from which no heat could escape. In actual practice where there are losses from conduction and radiation, the temperatures would be much lower. It will be seen

from this, how a careless fireman not able to control the combustion properly can readily cause a great wastage of fuel more particularly in the case of the higher temperatures.

5. The remaining loss of heat is due to conduction through the walls and radiation from their surface. A great deal also is absorbed by the ground, particularly if the latter is damp.

These five points account for the loss of 97 percent of fuel, and any improvements that can be brought about in them will lower the expenditure of fuel. But beyond this, there is a very important saving to be effected. In order to remove fired goods from the oven, the whole of it and its contents have to be allowed to cool down to such a temperature that men can enter and handle them. The result is that practically all the heat, which has been accumulated at so much expense, is allowed to escape without being utilized. The recuperation of this heat by drawing the air of combustion over the fired goods, so that it becomes heated up to their temperature before being used can evidently lead to a considerable saving in fuel. If all the heat of combustion were available for heating up the goods, this saving would be of the order of 25 percent. In order to completely burn 12 grams of carbon, 32 grams of oxygen are required which are contained in 144 grams of air. If this air is used at 1070°, the heat added to the actual heat of combustion of the carbon is $144 \times 1050 \times .24 = 36.28$. This corresponds to the heat of combustion of $\frac{36.280}{8080} = 4.49$ grams of carbon. It follows that with recuperation, as much heat is obtained from the combustion of 12 grams of carbon as is obtained from 16.49 grams where there is no recuperation, *i. e.* there is a possible saving of 27.25 percent of the fuel. The advantage is, however, even greater than this; the extra heat brought in by the air goes towards making the flame hotter, so that a much larger proportion of the heat developed is available for heating up the goods before the gases escape.

It has long been realized that it should be possible to fire with a much smaller fuel consumption by converting the operation into a continuous one, the air used for burning the fuel being drawn through the cooling goods and so recuperating their heat,

and the products of combustion being drawn through the unfired goods so as to give up their heat as fully as possible before escaping into the atmosphere. There are two different types of oven working on these lines.

Ring Ovens. These ovens of which the Hofmann brick kiln can be selected as a type, are generally oval in shape and are divided into a number of chambers which are fired successively, the zone of heat traveling round the oven. The fuel is dropped amongst the goods in the chamber which is being fired, and is there burnt with air heated by being drawn through the cooling chambers, whilst the products of combustion are drawn through several chambers ahead of that actually being fired and then into the shaft. This system has certain obvious defects:

(a) As the fire zone advances, fresh portions of the oven wall, which is very thick, have to be heated up; in this way, a large amount of heat is taken up which can only be partially recovered.

(b) The fuel is allowed to drop amongst the goods, and a considerable portion of them are spoilt, so that only common bricks can be economically fired in this way.

(c) Fuel is scattered here and there amongst the goods in the chamber which is being fired. A great amount of the air, which is drawn through the chamber, does not come into contact with it at all; as a result, a very large excess of air has to be used. Professor Seger puts the figure at 6 to 10 times the amount actually required.

(d) The heat is not evenly distributed, the top of the oven is always hotter than the bottom.

Tunnel Ovens. The second principle of continuous firing is that of the tunnel oven. The fuel is here burnt in the center of the tunnel, and the gases are drawn off towards one end. The goods travel in the opposite direction on trucks, and the air to burn the fuel is drawn through them. The zone of heat is thus stationary, and when the condition of steady running is reached, no further heat is taken up by the walls.

A great many attempts to construct ovens of this type have been made, but in general without much success. In the Dinz

oven as in the Hofmann kiln, the fuel is dropped upon the trucks amongst the goods at the hottest place. This is necessarily a dirty method, the trucks become littered with ashes, and it is exceedingly difficult to work it satisfactorily. The Faugeron oven has now been in existence for about 15 years; in certain cases it has the advantage over the Dinz oven of being gas fired. Very elaborate precautions have been taken to direct the flames to the base of the goods by means of screens attached to the trucks. Notwithstanding this, the temperature differs very much from place to place, the top being always hotter than the bottom. There is the same difficulty in both these tunnel ovens as in the Hofmann kiln, namely, that the air used for combustion, when drawn through the zone where the fuel is burning, does not necessarily come into contact with the latter, and a large excess has to be used.

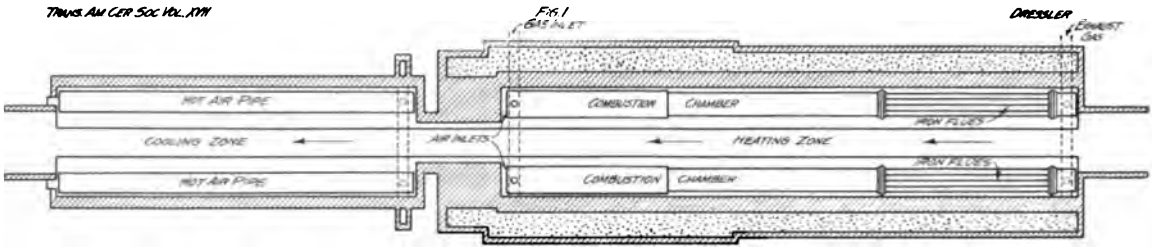
All the continuous ovens so far considered, whilst saving very largely in fuel, have not yet proved a great commercial success for the following reasons:

1. There is a tendency to reduce and sulphur the ware at the point of entry of the gases or fuel, *i. e.* near the hottest point, and the avoidance of this calls for great skill on the part of the fireman.

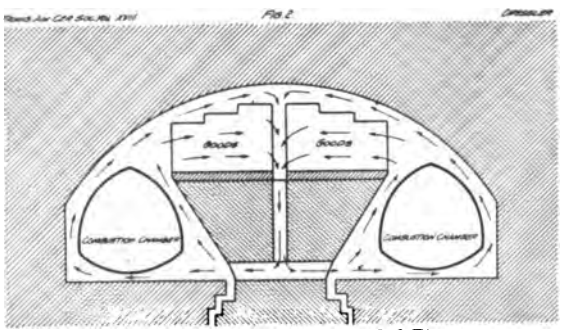
2. The distribution of heat in the goods is very uneven, the oven being always much hotter at the top than at the bottom in spite of the most elaborate devices to bring the heat down.

Thus, although these systems show great economy, yet they retain all the difficulties and disadvantages of the older ovens, perhaps even in an intensified form, and as a result a certain prejudice against tunnel ovens exist so that this system of firing has not made much progress.

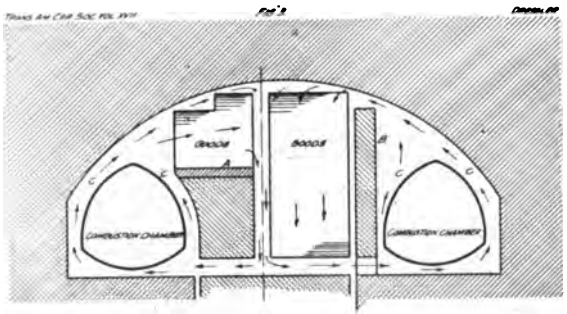
The latest continuous kiln is the Dressler Tunnel Oven. This can claim all the economies in fuel which a tunnel system brings with it, combined with certainty and equality of firing that no other oven can approach. It is upon this fact that its success rests, and, as will be shown later, the actual saving due to the goods being uniformly of first quality probably exceeds the maximum possible economy in fuel.



Diagramatic Plan of a Dressler Tunnel Oven



Diagramatic Section of a Dressler Tunnel Oven



In the Dressler tunnel oven, an entirely new principle of continuous firing is introduced, the flames not coming into contact with the goods at all. Essentially, it consists of a tunnel which can be divided longitudinally into two portions: the heating zone which occupies rather more than half the length, and the cooling zone. In the heating zone, the oven is covered with a thick layer of insulating powder which prevents the escape of heat through the walls. Inside this portion, there are two lateral tubes placed on either side of the oven and running towards its mouth. In the simplest form, these tubes have a triangular section and are built up of sets of three pieces corrugated transversely to their length in order to increase the surface and also to give greater strength to resist the tendency to bend at a high temperature. The gases are burnt in these tubes which are known as the "combustion chambers." They are entirely independent of the structure of the oven and are supported upon cradles placed at intervals and which are free to move on a flat bench covered with a thin layer of sand. Thus all disruption due to differential movement of the combustion chambers and the oven proper during heat and cooling is avoided.

Figures 1 and 2 show a diagramatic plan and section of an early type of Dressler tunnel oven. For the sake of clearness in Figure 1, the scale of the length of the oven is half that of the breadth.

The Dressler tunnel oven resembles a muffle, in so far that the flame is screened from the goods, but differs from it in the very important feature, that there is no structural connection between what corresponds with the inner and outer walls of the muffle. In order to emphasize this freedom of movement the combustion chambers have been described as "floating."

The first portion of this chamber is of a special very highly refractory material, the middle portion, which does not have to stand such elevated temperatures, of a less refractory material, and the coolest portion consists of a series of iron pipes which throw off the last portion of the heat very readily. The end of the chamber is connected with a fan so that a constant draught regulated by means of a damper is maintained.

The oven is fired with producer gas which is prepared from any gasifiable fuel, or, when it is available, natural gas may be used. The gas is admitted in the middle of the oven to the combustion chamber and is there burnt with hot air drawn over the cooling goods. The burning gases are sucked along the combustion chamber towards the mouth of the oven, the goods placed on trucks are propelled through the oven in the opposite direction and so are very gradually heated till the portion of the chamber is reached where the gases are burning. Beyond that point, the temperature is stationary for a while, and then the goods begin to be cooled by the air used to burn the gases.

A water gauge is attached to the combustion chambers near the point of entry of the gases, and the pull of the fan is so adjusted, that there is always a depression equal to about 1/32nd of an inch of water in the chamber. This is sufficient to prevent the passage of any gas from the chamber into the oven proper. If there is any exchange of gases through the cracks which are inevitably present, it is from the oven to the combustion chamber. In this way, the oven is kept entirely free from gas and from the products of combustion, and all action of the gases upon the goods is obviated. The most delicate ware can simply be placed on light shelves unprotected by saggers. This leads to a great lessenning of the gross weight of material to be fired for a given net weight of goods. In the case of the up-draught kiln we were considering, the weight of the saggers is nearly four times that of the goods they contain. By means of the Dressler tunnel oven, it has been found possible to fire jampots to 1250°C. upon shelves and supports which only weigh just as much as themselves, so that in this way, there is effected considerable economy in fuel. Moreover, the expense of the saggers, which have a very limited life, is removed.

Both the gas inlet and the air inlet are controlled by sliding dampers and can be adjusted with the greatest nicety, so much so, that it has been found possible, by working carefully, to obtain regularly an exhaust gas containing 18 to 19 percent of CO_2 in actual commercial running.

The greatest step forward in the Dressler tunnel oven is,

however, in the system by which the heat is communicated from the gases to the goods. The passage of heat from one spot to another can take place in three different ways: by conduction, by convection, and by radiation.

(a) Conduction. The heat is transmitted directly from particle to particle, the particles not altering in their relative positions to one another. The rate at which heat travels from one spot to another depends upon the distance, the difference of temperatures and the thermal conductivity of the material. Now, the conductivity of fireclay is very low, and as a great deal of the equalization of heat throughout the ordinary intermittent oven depends upon conduction, it is very slow. This necessitates a long "soaking heat" which involves a large expenditure of fuel.

(b) Convection. The heat in this case is carried by the actual motion of a fluid, in the case of an oven of air or gas. The motion is due to the fact, that on heating a fluid, it expands and, becoming less dense, tends to rise; on cooling it becomes more dense and falls. It is upon this principle that the central heating of houses depends.

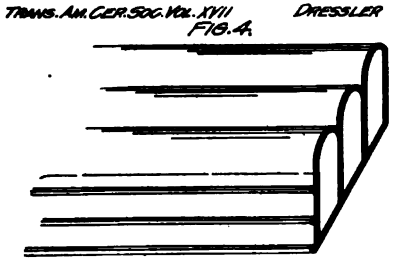
(c) Radiation. The heat passes across an intervening space in the same way that energy finds its way from the Sun to the Earth, almost instantaneously.

In the Dressler tunnel oven the purpose has been to secure the greatest possible efficiency by adjusting matters, so that the passage of heat takes place under the most favorable conditions for the working of the oven.

The heat from the gases has to get through the chamber wall by conduction. There is every advantage in making the walls as thin as possible, and further the thinner they are the better the chambers stand. This at first sight appears paradoxical; but the thicker the chamber wall, the greater the difference of temperature has to be between the inside and outside in order that enough heat may be able to get through to heat up the goods. Thus the thicker the chamber, the hotter it has to be inside and the more it gets punished, and the sooner it perishes. From the point of view of fuel economy, there is also an advantage in making the chambers of material of the highest possible conductivity.

Once the heat has got through the combustion chamber wall, the aim has been to carry it from the hot wall to the cooler goods entirely by convection, cutting off radiation as far as possible. The air round the combustion chambers is heated and rises to the top of the oven. Here, it meets the goods, is cooled and drops down channels provided in them and the trucks. At the level of the base of the combustion chambers, the air passes out through ports and is once more sucked up round them. The goods are thus continually bathed in a stream of pure hot air which, as has been seen, cannot be contaminated, so long as the fan continues to draw.

In the earlier type of the Dressler tunnel oven, the combustion chambers were built up of fireclay pieces made as described above, as thin as possible, in order to facilitate the passage of



heat. Those at the hottest point naturally were considerably hotter than the goods required to be and so tended to roast the outside portions nearest them and leave the center cooler. In order to cut off this radiant heat, a screen had to be interposed. This was first made part of the trucks. The goods were placed at the top of the oven above the level of the combustion chamber, and the radiation from the latter was cut off by a thick slab (A) — Fig. 3 — on which they rested. This gave great uniformity of firing, but it had the disadvantage of reducing very greatly the space available for ware. Moreover, there was a very heavy superstructure to the truck which had to be heated up as well as the goods and their actual supports. In spite of this, the saving in fuel was found to be of the order of 75 percent on muffle practice, and yet it amounted to not less than 17.5 percent of the weight of the goods and supports fired to 1050°C.

The next step was to place a screen by the side of the combustion chamber in the form of a wall, (Fig. 3) (B), with ports at the base at the level of the bottom of the combustion chamber to allow the free passage of circulating air. It was now possible to fire up the truck, completely filled with goods from the level of the base of the combustion chamber upwards, and immediately the economy was very largely increased while the uniformity of firing was maintained.

The final modification of this idea was to make the screen part of the combustion chamber itself, and with this the greatest success has been obtained. The chamber is built up of double walled pieces shaped like long hollow bricks, (see Fig. 4); the outer wall serves to cut off the radiant heat from the goods. In the space between the two parallel walls, the current of air is very greatly intensified, so that the circulation is much improved, and the goods are fired with great uniformity to the very bottom. By this means, it has been found possible to fire to 1050°C. with a proportion of 5 to 6 percent of fuel to the weight of goods, and to 1250°C. with from 10 to 12 percent, *i. e.* fine ware is being fired with an expenditure of fuel not greater than that of the Hofmann brick kiln working under the best conditions. Figure 5 shows a section of this latest type of oven.

The use of these cavity chambers also made it possible to get over the difficulties which were experienced in reaching the highest temperature required in pottery. It was found that all the best refractory materials, of which the combustion chamber could be constructed, softened at a temperature very far below that at which they actually melted. When it was attempted to fire an oven beyond 1150°C. with single wall chambers, the latter necessarily became much hotter right through than the goods required to be, they softened and, even when they had deep corrugations, were no longer able to support their own weight and gradually collapsed. But in the case of the cavity chambers, the intense circulation of air keeps the outer wall and the ribs connecting it with the inner wall down to the temperature of the goods or very little above it. At this temperature, the fire clay remains perfectly rigid, the inner wall becomes hotter and softens but is

Trans. Am. Cer. Soc. Vol. XVII FIG. 5. DRESSLER

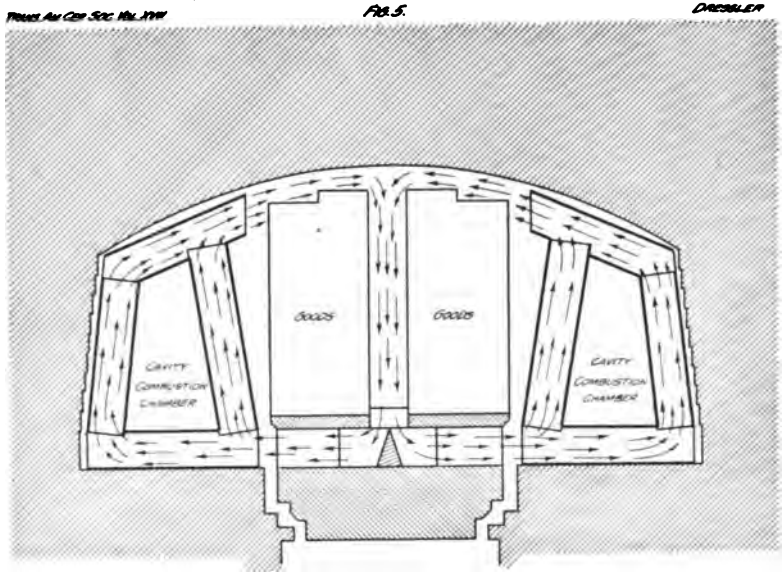
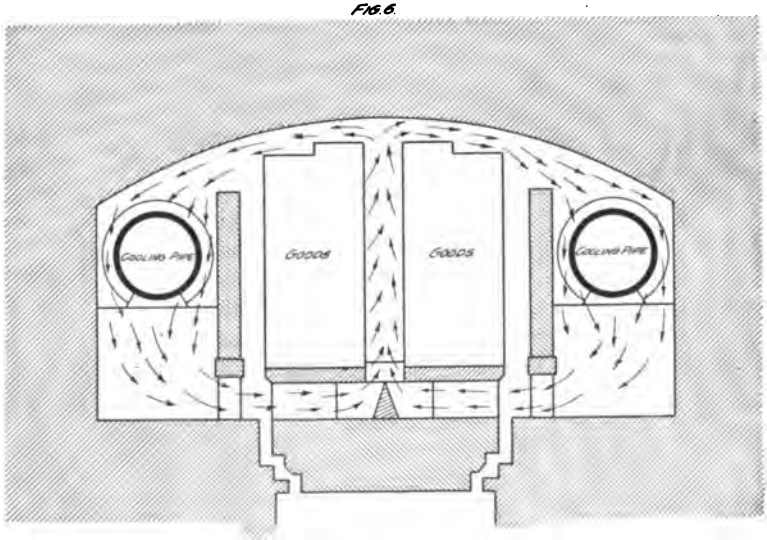


FIG. 6.



prevented from collapsing by its attachment to the stiffer ribs of the outer wall. It is as if a thin sheet of lead, not strong enough to keep itself from falling in, were supported by a stiff framework of channel iron.

It may be interesting to consider a little more fully, how it is, that this system of firing by convected heat leads to a great uniformity of temperature throughout the mass of the goods. In the case of the ordinary oven, when the flame has made an upward path for itself amongst the saggers, this path or flue becomes hotter and draws more and more. As a consequence, it is exceedingly difficult to shift the flame to another and cooler spot, and it calls for great skill on the part of the fireman to create an even distribution of heat throughout the oven. With the Dressler tunnel oven, the opposite is the case. The firing is conducted by means of a falling stream of hot air. The cavity combustion chambers deliver a great volume of hot air to the top of the oven at a temperature very slightly above that at which the goods are to be fired. As the goods are not as hot as this, the air is cooled and immediately falls, its place being taken by fresh hot air from the chambers. The rate of fall, anywhere, depends upon the difference in density between the hot air at the top of the oven and the cooler air at the sot in question, *i. e.* on the difference in temperature. The greater this difference, the more rapid and concentrated is the stream. Thus the effect is automatically to heat up any spot which may be cooler, until it has the same temperature as the goods round it. By the above described mechanism, the zone of the goods at the same temperature as the stream of air delivered to the top of the oven gradually becomes deeper and deeper, until the whole mass is evenly fired, the circulation of air being finally maintained by the difference in temperature between the very base of the truck and the flues in the combustion chamber. The regular firing is thus not dependent upon the skill of the fireman but is an inherent quality of the oven.

The cooling of the goods is accomplished in much about the same fashion as the heating, and is equally gradual; only the goods are now hotter than the oven itself, and the air instead of

falling amongst them rises through them till the top is reached. It is now cooled by the walls of the oven and drops down till it reaches the base of the truck and is then once more sucked up the channel provided. Since the air is being pulled along into the combustion chamber, there is not a continual circulation of the same air as in the heating zone, but the cold air which enters at the exit end of the oven pursues a spiral path until it reaches the entrance to the chamber where it is drawn in. At no point do the hot goods come suddenly into contact with cold air, and the dunting, which is a great source of loss in other tunnel ovens, is quite eliminated, although the ware is not protected by saggers. It will be observed in Figure 6 (which shows a section of the cooling zone) that a cooling pipe is present. The necessity for this was not at first realized, but it was found impossible to cool the goods completely with the air required exactly to burn the gas needed to fire them. The specific heats of air and fire clay are very nearly equal, so that if one truck per hour passes out of the oven, an equal mass of air has to be heated up to the temperature at which the goods are fired, in order that the latter may emerge cold. The quantity of air required to burn the gas is, however, only about one-quarter of this. It is uneconomical to draw an excess of air into the combustion chamber, since this would cool the flame, and actually more gas would have to be used to reach the temperature. Thus there is a limit to the heat which can economically be recuperated for burning the gas. It was found possible, however, to recover the remainder of the heat by running a pair of pipes on either side of the oven in the cooling zone, from the exit end to a spot about 12 feet from the entrance to the combustion chamber. Through these pipes, cold air is drawn, and cooling the goods and becoming heated as it passes along the oven, it is sucked off and utilized for drying or pre-heating. In this way, there is placed at the disposal of the manufacturer a supply of heat equivalent to say half the fuel burnt in the oven for absolutely no additional cost.

It may be of interest to sum up the advantages which can be claimed for the Dressler tunnel oven over ordinary intermittent methods of firing as follows:

1. The zone of heat is stationary, hence there is no alternate heating or cooling of the oven structure. This represents a large saving in fuel and also in repairs. The structure of the Dressler tunnel oven may almost be said not to suffer at all, the only parts that require occasional renewal being the combustion chambers and the repairs are then limited to a few feet at the hottest point.

2. The exhaust gases are drawn off fairly cool (about 200-250°C.).

3. The heat of the cooling goods is recuperated for burning the gas. Beyond this, there is a supply of pure hot air equivalent to more than half the heat generated in the oven and costing nothin in extra fuel.

4. The oven is very easily worked, no specially skilled firemen are required to obtain good results. The firing operation is controlled by Seger cones placed on the trucks or by a recording pyrometer. If the temperature is found to have a tendency to rise, a little less gas is allowed to enter, and if the heat is falling, the dampers are opened and more gas is burnt.

5. The atmosphere is kept entirely free from gases by the fan. The pull of this is observed in the water gauge attached to the chambers. If, in the course of time owing to the development of cracks in the latter, the suction is found to fall off, it is only necessary to open the fan damper a little further.

6. No saggers are required to protect the goods, this is in itself an economy, and further, it reduces the cost of firing a given net weight of goods.

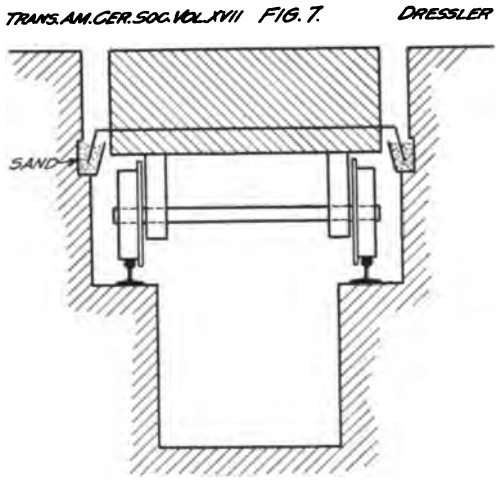
7. The even distribution of heat is automatically effected, all the goods being fired to practically the same temperature.

8. The losses from dunting are reduced to a vanishing point.

There are two further points which appeal more particularly to the commercial side of a pottery.

9. Owing to the above mentioned regularities, there are no seconds. It is perhaps not fully realized what a great saving there is to be effected by practically doing away with seconds. In the firing of tiles in glost in the Dressler tunnel oven, it is found that 95 percent come out perfect, the remainder suffering

from defects not directly attributable to the working of the oven, but being faults in the biscuit or grains on the surface derived from the supports. One of the larger English tile works produces about 3550 square yards weekly, 2640 being white and 910 colored enamel. It is found that in the firing of the white tiles, 25 percent turn out seconds and are worth 2 shillings less per yard than the firsts; of the colored enamels, 15 percent are seconds, involving a loss of 3 shillings 6 pence per yard. In the case of the white tiles, the difference between the proportion of seconds when fired by the old method and in the Dressler tunnel



oven is 25 percent—5 percent=20 percent. Similarly for the colored enamels this difference is 10 percent.

WHITE

20 percent of 2640=528 @ 2/-.....£ 52.16.0.

COLORED ENAMELS

10 percent of 910= 91 @ 3/6..... 15.18.6.

£ 68.14.6. per week

£3574. 0.0. per year

Although the savings in fuel are very important, this figure which represents the saving due to the goods being of first quality is even larger.

10. There is no need to keep a large stock when goods can be fired in glost in about 30 hours and can then be taken direct from the truck, packed, and sent off. Orders can be executed within 48 hours of their receipt.

The above points indicate that here again, as so often happens where a new principle is brought into play, the direct advantages sought for and realized are accompanied by many kinds of parallel results, sometimes unexpectedly favorable. Whilst aiming mainly at a scientific utilization of heat, it was found that this could not be accomplished excepting by strictly enclosing the burning gases and controlling their rate of flow, at both ends of the combustion chamber. This control of the gases gave a control of the atmosphere in the oven and of the temperature and therefore of the quality of the goods, and it also enabled the rate of heating and cooling to be regulated, thereby ensuring against another of the potters' troubles, namely, firecracks and dunting.

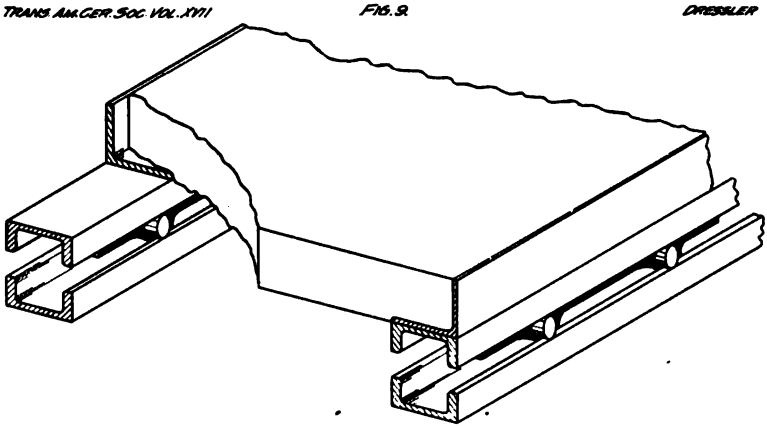
Besides the pottery problem which deals with the application of heat to clay ware, we have, necessarily, an engineering or mechanical problem, since it is necessary to convey goods to be fired to a place where the heat is far in excess of that which metal can stand, and yet where trucks of iron or steel must be used. Obviously, pottery does not possess the qualities of toughness and tensile strength needed for wheels, rollers, rails or truck frames.

In previous tunnel ovens, the constructors endeavored to screen the mechanical parts away from the goods by means of iron plates, dipping in sand troughs. (See Fig. 7.)

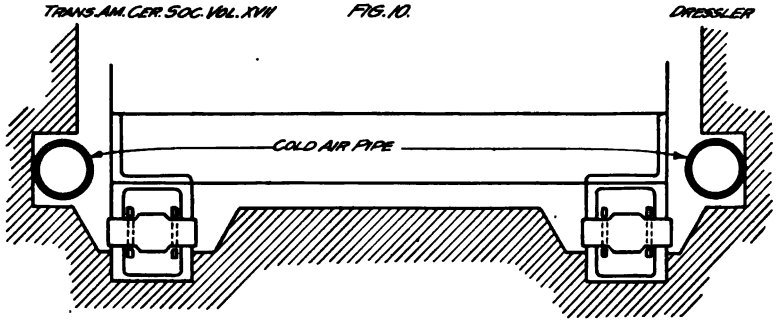
In this way, it was hoped that the wheels would remain sufficiently cool to make it possible to lubricate the axles, and, in effect, by keeping a large air chamber below the axles in which cold air could circulate, the temperature was kept sufficiently cool so that lubricants would not be burnt away. Mr. Dressler preferred to get rid of the problem of lubrication by adopting rollers in lieu of wheels. These, it is well known, move without

TRANS. AM. CER. SOC. VOL. XVII FIG. 8. DRESSLER

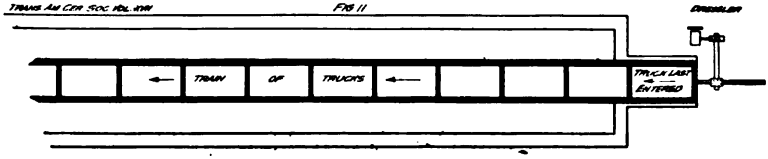
TRANS. AM. CER. SOC. VOL. XVII FIG. 9. DRESSLER



TRANS. AM. CER. SOC. VOL. XVII FIG. 10. DRESSLER



TRANS. AM. CER. SOC. VOL. XVII FIG. 11. DRESSLER



friction and therefore the interposition of lubricants is unnecessary. He adopted a form of independent links, each holding two rollers, maintained at a distance of about 10 inches apart. (See Fig. 8.)

These rollers run in steel channels, (Fig. 9), two such channels being laid down as rails throughout the oven, and a corresponding two being fixed to each truck and acting as runners, engaging the rollers from above, while the rail channels do so from below.

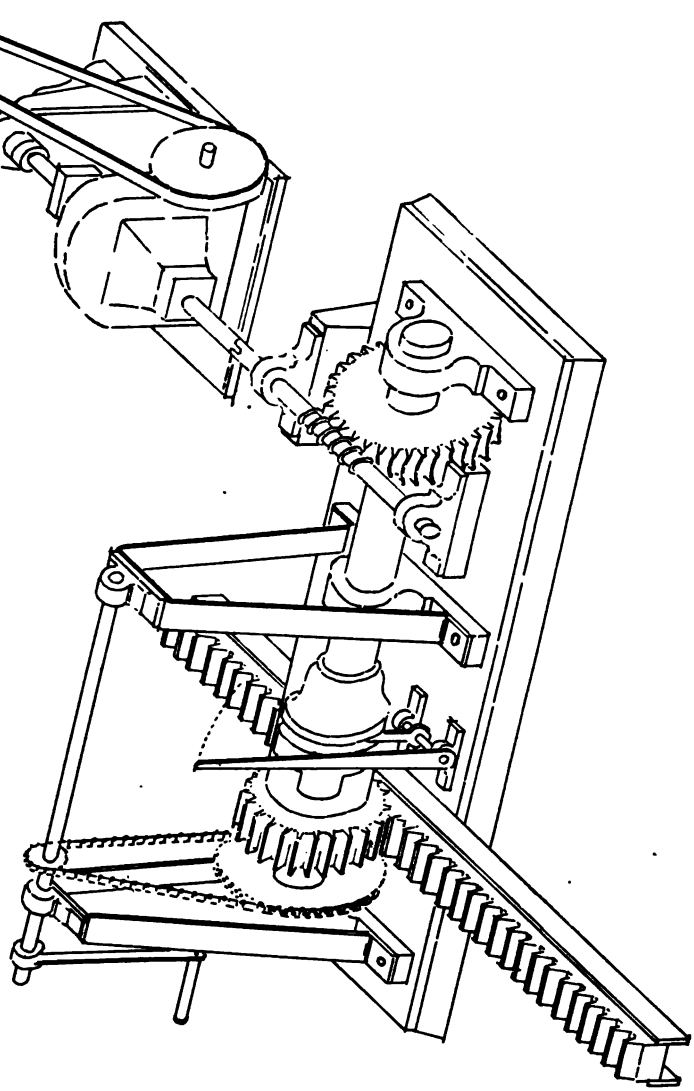
Having dispensed with both the sand troughs and the subtunnel, on the ground that the rollers might become hot, without stopping the progress of the trucks by gripping or binding, as would be the case with wheels, it was nevertheless desirable that they should not become so hot that the iron would scale or be deformed. This danger was avoided by drawing off any excess of heat by means of cold air pipes running alongside the frames. (See Fig. 10.)

These pipes are connected up to the flue fan, and maintain a low temperature at even the hottest point, never for instance exceeding 300 to 350 degrees Centigrade. It must be stated also, that there is every tendency for the heat to remain in the upper zone of the oven section, where a vigorous circulation keeps it from penetrating below. Radiant heat, of course, is screened off.

The train of trucks in the oven is caused to move continuously, being pushed by the last truck introduced into the antechamber. (See Fig. 11.)

The pushing is done by an ordinary rack, which is acted upon by a toothed wheel geared down by means of reducing gears, so that the progress should not exceed one inch per minute. (Fig. 12.)

A clutch enables the rack to be put in or out of gear as desired, and a crank, which is actuated by hand, enables the operator to bring the rack back into position, after the mechanical propulsion of each truck has been completed. A small electric motor using no more than 1/32 H. P. will push a train weighing 200 tons.



DRESSLER

FIG. 12

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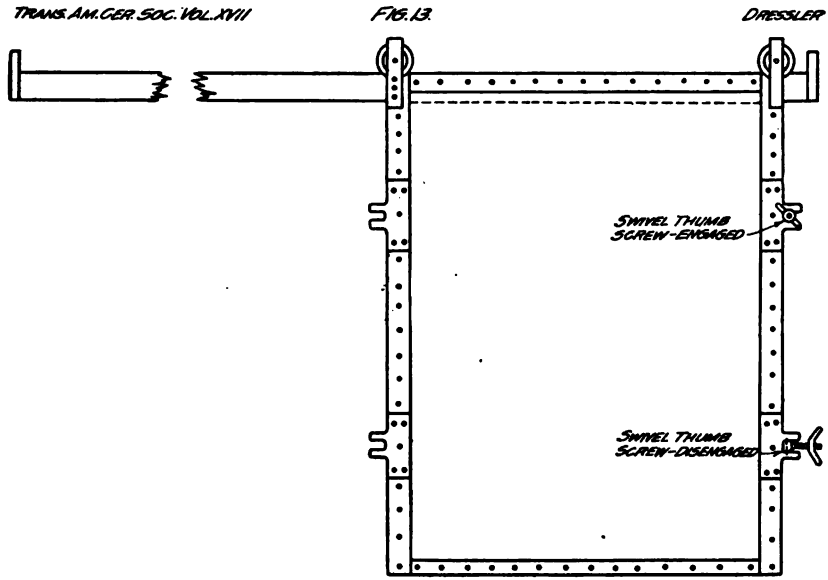
The doors are of the sliding type and are made of thin sheet steel. They hang loosely on wheels, but are kept tightly in position when closed by means of movable lugs provided with thumb screws. (Fig. 13.)



The fan is an ordinary water cooled exhaust fan and requires no special description. Two to three H. P. will drive this fan.

The producer is generally of the ordinary Siemens type and calls for no special description.

NOTE ON ESTRICH PLASTER

BY R. K. HURSH, URBANA, ILL.

In the literature on gypsum, its modifications, its products and their properties, there is considerable contradiction and conflicting evidence. The extensive studies of van't Hoff[1] and his associates show the complexity of behavior and the difficulty of obtaining definite data by ordinary experimental methods. In these studies, which were made in connection with an investigation of the Stassfurt salt deposits, some very excellent data has been obtained upon the modifications of gypsum at low temperatures. Four modifications of gypsum are identified.

1. Natural gypsum ..... $CaSO_4.2\,H_2O$
2. Natural anhydrite ..... $CaSO_4$
3. Hemihydrate ..... $CaSO_4.\frac{1}{2}\,H_2O$
4. Soluble anhydride ..... $CaSO_4$

The first two occur naturally, the dihydrate forming the raw material for the plaster industry, the anhydrite being found in greater or less amount in all deposits. The hemihydrate is formed by heating the dihydrate to 107°C. or slightly above for a considerable time. Commercially, temperatures up to 200°C. or above are used but for short periods of time.

The fourth form is obtained by overheating plaster somewhat in burning, or it may be prepared by treating hemihydrate with an excess of water, decanting after standing for a time, drying and heating to 100°C. The soluble anhydride has the power of taking up water much more vigorously than the hemihydrate and sets even more rapidly.

The hemihydrate seems to be an intermediate product between the dihydrate and the soluble anhydride. When ordinary plaster is burned to a temperature above 150°, or when the heat treatment is prolonged, the hemihydrate begins to decompose to form soluble anhydride. W. A. Davis[2] states that this compound is extremely hygroscopic and rapidly absorbs 7-7½ percent of

[1] *Sitzber. d. Berlin Akad. Wiss.* 1900, 1901, 1908.
[2] W. A. Davis, *Jr. Soc. Chem. Ind.* (1907) 26, 727.

moisture, part of which goes to re-form hemihydrate, and a part is retained mechanically.

It is shown by van't Hoff[3] that the hemihydrate is a metastable form and may change even at low temperatures according to the equation,

$$4\ CaSO_4.\tfrac{1}{2}\ H_2O \rightarrow CaSO_4.2\ H_2O + 3\ CaSO_4$$

This probably accounts for the fact that plaster, which has been aged, does not require as much water in preparing for mold casting. One experiment shows that fresh plaster required 91 percent of its weight in water, after four weeks only 72 percent, and after three months only 59 percent.

When heated above 200°C. for some time, gypsum becomes completely dehydrated, and the time required for its re-hydration is very much increased. However, heating for short periods of time at temperatures even in excess of this does not seriously reduce the setting properties. The anhydrous calcium sulphate formed above 200° is generally termed the No. 1 anhydride. When heated for long periods of time at 200-300° or for short periods of time at somewhat higher temperatures, the product becomes dead-burned. It will hydrate very slowly but gives no real hardening reaction and is therefore of no technical value.

At a somewhat higher temperature of heating, there is developed a further modification of the anhydrous sulphate termed variously the "b" form, the No. 2 anhydride, or Estrich. Its properties are very different from those of the preceding modifications. Unlike the dead-burned anhydride, it has the ability to hydrate and harden, forming an extremely dense, hard cement. Its rate of hydration and setting is very much slower than that of the hemihydrate, several hours being required, and full strength is developed only after weeks. The strength developed by estrich is exceedingly high, comparing well with that of Portland cement. It is largely used as a flooring material. Its hydration proceeds without perceptible heating and the setting without a change in volume.

The temperature at which estrich is formed is somewhat in dispute. It is too often confused with the alum plasters, the

[3] van't Hoff, Hinrichson and Weigert—*Sitzber. d. Berlin Akad. Wiss.* 1901, 577.

Scott or Keene's cements. Commercially estrich plaster is burned at 900-1000°C. and possibly higher. In laboratory study it may, without doubt, be formed at considerably lower temperatures, since the duration of heat treatment is an extremely important factor in such cases.

In continuation of his studies on the modifications of gypsum at the lower temperatures, van't Hoff[4] attempted a study of the hydration process and the influence of burning temperature on the hardening of estrich. By analysis, he found a commercial estrich to conform practically to the anhydride of $CaSO_4$, there being about 2 percent excess CaO. By means of the dilatometer study, he found that the hydration corresponded to the formation of the dihydrate, $CaSO_4.2\,H_2O$, about 21 percent of water being taken up. Crystalline hemihydrate was heated for ten hours at 200, 300 and 400° respectively, and the process of hydration studied by means of the dilatometer and by noting the absorption of H_2O in a moist atmosphere. The results showed a decreasing ability to hydrate with increasing burning temperature. A further study of the influence of crystal form on the ability to hydrate showed a greater tendency to combine with water when a crystalline structure remained after heating. His conclusions are, that ability to hydrate decreases as the burning temperature is raised, and that the retention of a crystalline form in the burned product is of great importance in respect to hydration. No evidence was obtained that a higher heating gave a product with an ability to set.

The temperature range covered in this work is too low to establish definite conclusions as to the product formed at the temperatures of estrich burning.

Rohland's[5] work shows that the first anhydrous modification of $CaSO_4$ may be obtained by long heating at 200-300°C. It has the ability to hydrate but not to harden. Its reaction velocity may be increased by addition of certain electrolytes. At 525-600°, a new modification of the anhydride is obtained which hydrates and hardens and is also affected in its hydration by electrolytes. No chemical difference was found between these two

[4] van't Hoff and Just—*Sitzber. d. Berlin Akad. Wiss.* 1908, 249-258.
[5] Rohland—*Der Stuck und Estrichgips.*

forms of anhydrous $CaSO_4$, and Rohland suggests a probable physical-chemical isomerism as an explanation of the change in properties. The first or No. 1 anhydride may, according to Rohland, be changed to the No. 2 or hydraulic form by three methods:

1. Long heating at 525°C.
2. Action of + catalyzers.
3. Long aging of the No. 1 anhydride and a resulting change to the No. 2 form.

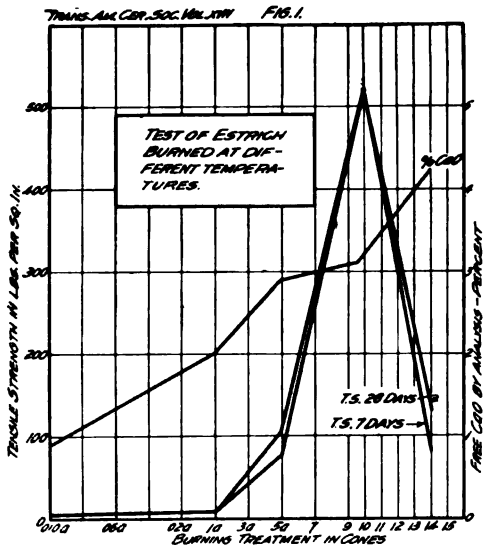
At 600°, Rohland finds the formation of a dead burned $CaSO_4$ without hydraulic properties.

Mueller[6] gives the temperature for formation of estrich as 800-900°. In his experiments, partial reduction of the sulphate took place, and he suggests the influence of the products of reduction as being a factor in the increased rate of hydration. An atempt to obtain an estrich by heating together natural anhydrite and CaO did not prove successful.

Glasenapp[7] has made a study of the properties of gypsum heated at different temperatures up to 1400°C. Up to 400°, the burned material would hydrate to form crystalline hemihydrate, the rate of the reaction decreasing with increased burning temperature. From 400-800°, there was practically no ability to hydrate and harden. Up to this temperature, he shows a retention by the particles of the crystalline form of the hemihydrate. From 800° up, there is a change in the appearance, the particles becoming more or less rounded and granular. Coincident with this change in the microscopic appearance of the particles, there appears the property of hydrating and hardening with the development of great strength. In other words, he finds that estrich is only formed at burning temperatures above 800°. The granular structure is taken as a criterion for true estrich, all products at lower temperatures being similar in appearance to the gypsum burned at 300° which is very slow to hydrate and shows little ability to harden.

At 800°, with four hour heating periods, the $CaSO_4$ began to dissociate showing about 3 percent CaO. At still higher temper-

[6] Mueller—*Untersuchungen uber Gips.*
[7] Glasenapp—*Studien uber Stuckgips, totgebrannten und Estrichgips.*


TRANS. AM. CER. SOC. VOL. XIV
FIG. 1.
TEST OF ESTRICH BURNED AT DIFFERENT TEMPERATURES.
% CaO
T.S. 28 DAYS
T.S. 7 DAYS
TENSILE STRENGTH IN LBS. PER SQ. IN.
FREE CaO BY ANALYSIS - PERCENT
BURNING TREATMENT IN CONES

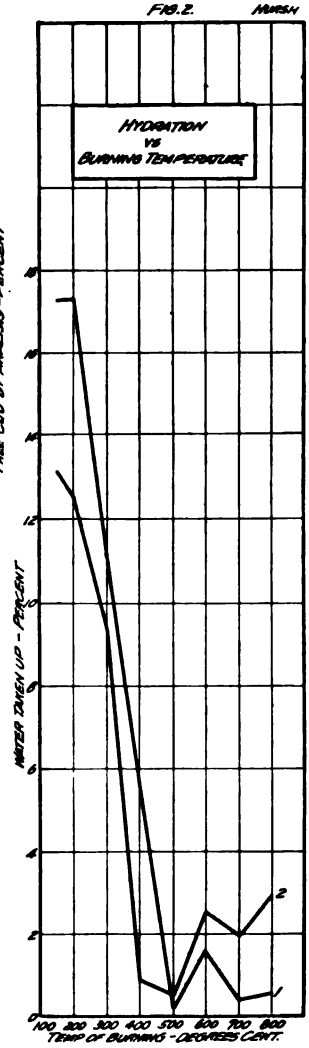


FIG. 2.
MARSH
HYDRATION VS BURNING TEMPERATURE
WATER DRIVEN UP - PERCENT
TEMP OF BURNING - DEGREES CENT.

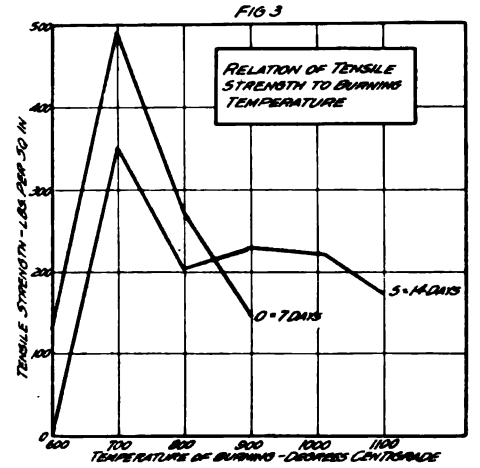


FIG 3
RELATION OF TENSILE STRENGTH TO BURNING TEMPERATURE
TENSILE STRENGTH - LBS PER SQ IN.
0 = 7 DAYS
5 = 14 DAYS
TEMPERATURE OF BURNING - DEGREES CENTIGRADE

atures, more CaO is found in the product. A sample burned to cone 12 in a porcelain kiln contained 83 percent CaO but still hardened well as estrich. Glasenapp concludes that estrich formation depends upon the production of a basic sulphate which appears at the higher temperatures as a glassy matrix surrounding particles of $CaSO_4$ which show the granular structure of estrich. The hydration, he finds to take place without change in form or volume, water being taken up in an amount equivalent to that of dihydrate but little or no crystallization occurring.

Glasenapp concludes that estrich is formed only above 800°, temperatures of 900° and upwards being the best in practice, and that overburning is practically impossible. The granular appearance under the microscope is taken as a positive means of distinguishing true estrich.

Cramer[8] notes that in burning gypsum, the specific gravity increases as the water is driven off up to 500°C., where the specific gravity falls but again rises with higher burning temperatures. Gypsum was burned at cones 015, 010 and 07, then mixed with water and the amount of combined water determined at the end of ten days. The results showed for cone 015 none, cone 010 10.6 percent, cone 07 5.4 percent. It was concluded that dead-burned gypsum was produced by underburning, and that overburning was possible.

In some work at the laboratory of the Tonindustrie Zeitung,[9] raw gypsum was burned at various temperatures, the products analyzed and tested for tensile and compressive strength. The results, as plotted in Fig. 1, show a marked increase in the hardening at cone 5 and a maximum strength at cone 10, while the amount of free CaO is increasing more or less gradually. There is no apparent relation between the degree of basicity and the strength developed in setting. Cone 10 seems to be the practical limit of burning of this gypsum to produce estrich. It was also shown in this work, that additions of $Ca(OH)_2$ to the estrich in amounts up to 10 percent materially increased the strength, but larger additions proved detrimental.

The effect of various burning treatments on the rate of re-

[9] *Tonind. Ztg.*, 37, 1904-5.

hydration of two gypsums is shown in Fig. 2. Small samples of the stone were calcined, the temperature being held at the points indicated for four hours in each case. Weighed portions of each batch were moistened and placed in a covered pan under a wet cloth for ten hours, after which time they were removed and dried to constant weight at 40°C. Various drying temperatures were tried, but in all cases the samples were completely dehydrated at temperatures above this point. The curve indicates that dead-burning has resulted at about 500°, and that higher temperatures show a marked increase in the ability of the material to hydrate. From these results, the best burning temperature for the alum plasters, if not for estrich, would seem to be about 600°C. Gypsum No. 1 is a very pure stone while No. 2 contains a considerable amount of impurities and is of a reddish-brown color when burned.

It is stated that not all gypsums are suitable for the production of estrich plaster. In *Das Kleine Gipsbuch,* properly burned estrich is described as having a reddish color. It is probable that certain impurities in gypsum are to some extent responsible for the development of the setting properties at the higher temperatures, or at least of influence on the temperature at which they appear.

The relation between the burning temperature and the strength of the plasters is shown for two gypsums **S** and **O** in Fig. 3. Sample **S** is a very pure rock, while **O** contains about 15 percent of impurities. A third sample was burned with the above two, but it did not harden sufficiently for testing. Portions of the rock were burned at every 100°C. from 600 to 1100, the temperature being held at the finish for five hours. The burned samples were then ground to pass the 100 mesh screen, mixed with water to such a consistency that water would just flush to the surface in trowelling and then made into standard tensile briquets. These were placed in a moist chamber under wet cloths for about 24 hours, removed from the molds and kept moist until tested.

The samples burned up to 800° showed considerable plasticity when wet but became sandy in character at 900 and above. This difference in the working properties of the mortars made

the establishment of a normal consistency by penetration methods, as with the Vicat needle, practically impossible.

The samples of both O and S burned at 600° showed a considerable amount of swelling when placed in the moist chamber, the increase in length of S-600 being about 17 percent, that of O-600 about half as great. These did not harden to any extent in seven days, and the briquets of S-600 remained soft for weeks. A portion of the soft material from S-600 was placed under the microscope with a little water and showed a slow crystallization of the dihydrate. No evidence of crystals was found in the higher burned samples. The only difference between this material and the ordinary stucco plaster seems to be in the rate of reaction with water. The swelling of the briquets in the moist chamber seems to be due to the development of the colloidal form which precedes that of the crystalline dihydrate. Some of the same briquets which were left for two months showed a subsequent shrinkage to nearly their original size.

In both samples, burning at 700° gave a plaster with the highest strength. It would seem that the best strength of estrich is produced at a considerably lower temperature than that which is given as used in practice. This may be due in part to the duration of the heat treatment, the same result being obtained here as at the higher temperatures and possibly more rapid burning in practice.

One of the important properties of estrich plaster is its constancy of volume in setting. No determinations were made on these plasters. It is possible that higher temperatures of burning are required to obtain this property, and that these are used commercially even at the sacrifice of some strength and quicker setting.

Further study of these products of gypsum should bring out more definitely the best burning temperatures, the influence of the various impurities upon the setting reaction, the constancy of volume in setting and the nature of the change in the gypsum which gives it setting properties at these temperatures. Such study may lead to the development of a more rapidly setting plaster with the same properties which would be of greater commercial value than estrich as now made.

THEORY OF THE ORIGIN OF CLAYS

BY WILBUR STOUT

The origin usually given for the underclays found in the coal measures is, that they were the muds of swamps purified by the action of the plant life that grew upon them. They were the soils. Since normal coal measure deposits are shales and sandstones, these soils then, when laid down, were necessarily of this character.

The origin of coal, most generally accepted is, that it was formed from vegetable matter deposited in swamps under conditions where only a partial dissolution or breaking up of the plant fiber took place, or where the forces of oxidation were not especially active. "The first step in the formation of coal is merely the formation and burial of peat of some kind, coal being recognized by most geologists as consolidated and metamorphosed peat."[1]

Clay and coal are related by depositive association at least, as both, in a general way, are swamp deposits. There is undoubtedly a close relation between the two for they occur as associated minerals with great regularity.

One of the striking features of the so-called pure clays is the constancy of composition, regardless of the horizons from which they are obtained. In them the silica-alumina ratio is in close agreement and it approaches that of the mineral kaolinite. The analyses in Table I bring out these features.

This constancy of relation is not a happen-so, due to local condition, for, as is shown by the analyses in Table I, this purity of material is found in a number of horizons; and in a given stratum, the same grade of clay may extend over a wide area, as is found for the Ohio-Kentucky deposits of Sciotoville clay or for the Pennsylvania deposits of Brookville and Mercer clays. Besides these kaolinitic types, there are many varieties of impure clays, grading from high aluminous kinds down to shales and

[1] White—David, "The Origin of Coal," *Bull. 38, Bureau of Mines*, p. 52.

sandstones, but since these are less characteristic, the discussion will be confined largely to the former types at present.

Clays appear to be the resultant of certain conditions which occurred as commonly as the preserving state under which the coals were laid down. The constancy of association and the interbedding of the two, common in many deposits, indicate that some of the conditions at least were constant during the entire period.

The analyses of the ash of 78 samples of coal and coke were made or collected by the author from other sources. Enough water is combined with the silica and alumina to form the mineral kaolinite, and the excess silica or alumina is also given. These are then reduced to 100 percent. The average of 73 of the 78 samples show kaolinite 85.85 percent, excess silica 14.17 percent; and for the remaining five samples, kaolinite 95.87 percent and excess alumina 4.13 percent. So figured, the kaolinite constitutes 90 percent or more of the total in 29 samples and 80 percent or more in 65 samples. These figures show, that the silica and alumina of the ash of these various coals are in such proportions that the mineral kaolinite could be formed, or that, at least, these components closely approach the ratio found in existing clays. For example, take the analyses of the ash of five coals[3] shows in Table II.

Taking the ash of sample No. 1 and combining water with the alumina and silica to form kaolinite which requires 12.46 parts, then reducing the total to 100 percent, it gives the following:

Silicic acid	52.30
Iron sesquioxide	1.86
Alumina	31.42
Lime	1.07
Magnesia	.61
Potash and soda	.96
Phosphoric acid	.12
Sulphuric acid	.21
Sulphur combined	.36
Water combined	11.09

[3] *Geol. Surv. of Ohio, Report* 1870, p. 232.

TABLE I

SAMPLE	No. 1	No. 2	No. 3	No. 4	No. 5
Silica, SiO_2	46.3	54.40	51.87	44.30	44.960
Alumina, Al_2O_3	39.8	41.19	43.21	38.31	38.172
Combined water or ignition loss	13.9	.....	.....	13.77	14.840
Ferrous oxide, FeO	....	1.35	1.86	.71	.....
Ferric Oxide, Fe_2O_3	....	.....	.....	1.40	.513
Lime, CaO	....	.08	.42	.82	.12
Magnesia, MgO	....	.32	.35	.59	.084
Manganous oxide, MnO	....	.01	.....	.10	.....
Potash, K_2O	....	.23	.31	.17	.071
Soda, Na_2O	....	.13	.19	.21	
Sulphur, S	....	trace	.....	trace	.....
Phosphorous pentoxide, P_2O_5	....	.11	.04	.....	.....
Titanic oxide, TiO_2	....	1.82	1.86	.....	1.240
Hygroscopic water	....	.....	.....	.75	.....
Silica / Alumina ratio	1.16	1.18	1.20	1.16	1.18

No. 1. Mineral kaolinite.

No. 2. Sciotoville clay, calcined, Scioto County, Ohio.

No. 3. Brookville clay, calcined, Clearfield County, Penn.

No. 4. Mercer clay, A. J. Wicke's mine, South Fork, Penn. *Bul. 447, U. S. Geol. Survey*, page 122.

No. 5. Sharon or Marshburg Upper Coal Clay, Barr and Radcliff mine, Elk County, Penn. *Professional Paper, No. 11, U. S. Geol. Survey*, page 214.

This in many respects compares favorably in composition to clays as shown by the following analysis:[3]

Silica	51.920
Alumina	31.640
Ferrous oxide	1.134
Titanic oxide	1.160
Lime	.030
Magnesia	.443
Alkali	.402
Water	13.490

The comparison shows about the same silica and alumina with only a small amount more of fluxing impurities in the coal ash. In fact, the ash from the above coal would be considered a fair refractory clay, as the silica and alumina are in a fair ratio, and the fluxing components well within the limits demanded for ordinary refractory materials. In sample No. 2, the iron oxide is entirely too high and the silica and alumina moderately low. In sample No. 3, the silica-alumina ratio compares favorably to that in the best clays, but the iron oxide, lime and phosphoric acid are high.

In samples Nos. 4 and 5, while the lime and iron oxide are high, the alumina is in excess of the kaolinitic ratio, in which respect, they much resemble the high aluminous clays of Kentucky. In samples Nos. 3 and 4, the ash is sufficiently low for them to be classed as pure coals, while in sample No. 5, the ash is remarkably low as it totals only .767 percent.

In the five samples of Table II, by considering only the alumina and silica and combining water enough to give kaolinite and reducing to 100 percent, it gives the results of Table III.

Reduced to mineral analyses they are as follows:

	No. 1	No. 2	No. 3	No. 4	No. 5
Silica	55.16	60.05	48.46	45.01	41.85
Alumina	33.14	29.53	38.10	41.48	45.60
Water	11.70	10.42	13.44	13.51	12.55

[3] *Prof. Paper No. 11, U. S. Geol. Survey*, p. 230, Sample No. 2.

TABLE II

	No. 1		No. 2		No. 3		No. 4		No. 5	
	PERCENT ASH	PERCENT COAL	PERCENT ASH	PERCENT COAL	PERCENT ASH	PERCENT COAL	PERCENT ASH	PERCENT COAL	PERCENT ASH	PERCENT COAL
Silicic acid	58.75	3.026	55.10	4.380	49.10	1.645	44.60	1.048	37.40	0.2888
Iron sesquioxide	2.09	0.108	13.33	1.060	3.68	0.123	7.40	0.174	9.73	0.0749
Alumina	35.30	1.819	27.10	2.155	38.60	1.293	41.10	0.965	40.77	0.3139
Lime	1.20	0.062	1.85	0.147	4.53	0.153	3.61	0.085	6.27	0.0483
Magnesia	0.68	0.035	0.27	0.022	0.16	0.005	1.28	0.030	1.60	0.0123
Potash and soda	1.08	0.056	1.00	0.079	1.10	0.037	1.82	0.043	1.29	0.0099
Phosphoric acid	0.13	0.007	0.41	0.033	2.23	0.075	0.29	0.007	0.51	0.0039
Sulphuric acid	0.24	0.013	0.58	0.046	0.07	0.002	0.58	0.014	1.99	0.0153
Sulphur combined	0.41	0.022	0.22	0.018	0.14	0.005	0.03	0.007	0.08	0.0006
Chlorine	trace	trace	trace	trace	trace	trace	.....	.....	.....	.....
Total	99.88	5.148	99.86	7.940	99.61	3.337	100.71	2.3667	99.64	0.7670

No. 1. New Straitsville coal, lower part of upper layer.

No. 2. New Straitsville coal, upper part of upper layer.

No. 3. Youghiogheny coal, Pa., Columbus Gas Works.

No. 4. Lower part of Jacob Sells' coal, Jackson County.

No. 5. Upper part of Jacob Sells' coal, Jackson County.

TABLE III

SAMPLE	ASH ANALYSIS		TO FORM KAOLINITE				REDUCED TO 100 PERCENT KAOLINITE				COMPOSITION	
	SiO_2	Al_2O_3	Al_2O_3	SiO_2	H_2O	EXCESS SiO_2	Al_2O_3	SiO_2	H_2O	EXCESS SiO_2	KAOLINITE	EXCESS SiO_2
	percent	*percent*	*percent*	*percent*	*percent*	*percent*	*percent*	*percent*	*percent*	*percent*	*percent*	*percent*
No. 1	58.75	35.30	35.30	41.53	12.46	17.22	33.14	38.99	11.70	16.17	83.83	16.17
No. 2	55.10	27.10	27.10	37.88	9.56	23.22	29.53	34.74	10.42	25.31	74.69	25.31
No. 3	49.10	38.60	38.60	45.41	13.62	3.69	38.10	44.82	13.44	3.64	96.36	3.64
						Al_2O_3				Al_2O_3		Al_2O_3
No. 4	44.60	41.10	37.91	44.60	13.39	3.19	38.26	45.01	13.51	3.22	96.78	3.22
No. 5	37.40	40.77	31.79	37.40	11.22	8.98	35.56	41.85	12.55	10.04	89.96	10.04

The analyses of 33 samples of clays picked at random and figured as the preceding coal ash, show kaolinite 80.48 percent, excess silica 19.52 percent and seven samples show kaolinite 95.68 percent, excess alumina 4.32 percent. In fifteen of the forty samples, the kaolinite constitutes 90 or more percent of the total, and in twenty-six samples, 80 or more percent. These figures thus agree very closely with those shown for the coal ash. The striking similarity in the amounts of kaolinite shown for the ash of the pure coals to the amounts shown for the best clays is of interest. In both cases, the kaolinite constitutes 90 or more percent of the total.

These figures show clearly, that by losing a few percent of fluxes, each of the samples of ash would become in composition practically what is shown by analyses for that of underclays. With oxidation of this vegetable matter in the presence of water or by leaching, at least a part of these impurities would be removed; iron oxide, lime, and magnesia would go out as bicarbonates, the sulphur as sulphates, the phosphorus as soluble phosphates, and the alkalies as soluble salts. So, from the above, it is shown that by removal of only a few percent of fluxes which would take place under oxidizing conditions, coal ash would be reduced to the composition of underclays.

Since the figures given show that coals when oxidized, leave clay-like ashes, agreeing with clays at least in the silica-alumina ratio and often in the total composition, it points directly to the conclusion, that the clays were laid down during periods in which the vegetable life in the swamps underwent a complete oxidation, while the coals were deposited during periods when a part of the vegetable tissue was preserved. In other words, there was no break in the plant life, only a change in the chemical conditions; clays representing oxidation periods, and coals representing preservative periods. In a general way, at present, oxidizing conditions are more common than conditions under which carbonaceous plant matter is preserved. For the present formation of peat beds, Davis gives the following:[4]

[4] Davis—Chas. A., *Bull. 38, Bureau of Mines*, pages 165-166.

"In present geologic time, peat is found in all parts of the earth where the conditions of moisture are favorable, but it is most uniformly present in regions where the rainfall is regular and abundant and the relative humidity of the air is constantly high. Abundant rainfall supplies the water necessary for preserving plant remains, and high humidity prevents excessive evaporation. As cool or cold air is much more readily saturated with water vapor than is warm air, the temperate and cold parts of the earth as a rule have more humid atmosphere than the warmer parts, and in this respect are favorable to peat formation.

"The form of land surface is also an important factor in determining the relative number of deposits of peat, especially in regions where rainfall is somewhat irregular, where the climate approaches dryness, or where hot, dry summers prevail or are somewhat frequent, as, for example, in North America in the greater part of the valley of the Mississippi and the southern part of the basin of the Great Lakes. In regions of this character, the presence of numerous depressions in which water may collect and stand permanently at a nearly constant level, and of poorly drained valleys or plains, largely controls the quantity of peat, because these depressions furnish places where accumulations of vegetable matter may be kept from desiccation and complete decomposition. In the Northern Hemisphere, the most recently glaciated parts of the continents furnish the most favorable physiographic conditions, and in North America, except for narrow strips along the coasts, the region of present-day peat accumulation is almost exactly coincident with the last deposits of the glacial period, known as the Wisconsin Drift.

"From climatic causes, the factors mentioned as favoring peat formation, are, in the present geological age of the earth's history, most generally present in the cold and temperate regions, but peat deposits of considerable extent also occur in the tropics, and even in the equatorial regions, wherever the climatic and physiographic conditions favor the accumulation and preservation of plant debris.

"It seems that two kinds of land surface are most suitable for the development of peat beds—gently sloping or flat areas and basins. In addition, a sufficient and regular rainfall and usually humid atmospheric conditions are essential in order that the surface of the plains may remain continually moist or wet, and the basins may be permanently filled with water."

Under the warm or temperate climatic conditions that existed during the Pennsylvanian coal forming epoch, the general tendency would be towards complete decay and non-preservation of the carbonaceous matter, for this is the common result under these climatic conditions at present. While peat forms here, the

beds are local and constitute only a small part of the total swamp area in which vegetation grows abundantly. Oxidizing instead of preserving conditions prevail. Even where peat forming conditions exist, slight changes may modify this so that complete decay of the additive or of the accumulated carbonaceous matter or of both would take place. Crustal movements, causing a slight elevation of the surface or even an arresting of the subsidence would tend towards oxidizing conditions. The shifting of currents, removal of barriers, periods of droughts, or any action causing a lowering of the pond waters, would lead to the same result. As stated by Davis, humidity changes may shift the action to one or the other conditions. Any current action bringing in a fresh supply of oxygen would lead to complete decay.

From present conditions, it seems evident that irregular and more or less differential subsidence took place during the formation of the coals, as these changes are now slowly but constantly taking place. The general character of the Coal Measures strata favor such changes. Further, the rock strata indicate that most of the coal forming swamps or ponds were quite shallow, so any slight change would effect the shore areas, if not the entire basin. The time required to build up a coal bed of some thickness, such as that of the important coal seams of the Pennsylvania series, even if the accumulation of carbonaceous matter was rapid, would be of considerable duration, evidently long enough for many minor changes to take place. Vegetable matter once oxidized was forever removed from that field for the original was not restored.

From general evidence, it seems as reasonable to believe, that there were variable periods of oxidation, when complete decay of the plant remains took place, as to believe that there were variable periods of preservation when the carbonaceous matter was preserved as coal. If the coals represent the latter conditions, then the clays are the resultant of the former.

The main points in the preceding discussion are as follows:

(a) That coals and clays are found as associated minerals with great regularity.

(b) That the evidence points to their deposition under somewhat similar conditions, *i. e.*, they were both swamp deposits.

(c) That oxidizing as well as preserving conditions existed during this swamp or coal forming period.

(d) That oxidation of coals give residues or ashes of a clay-like composition.

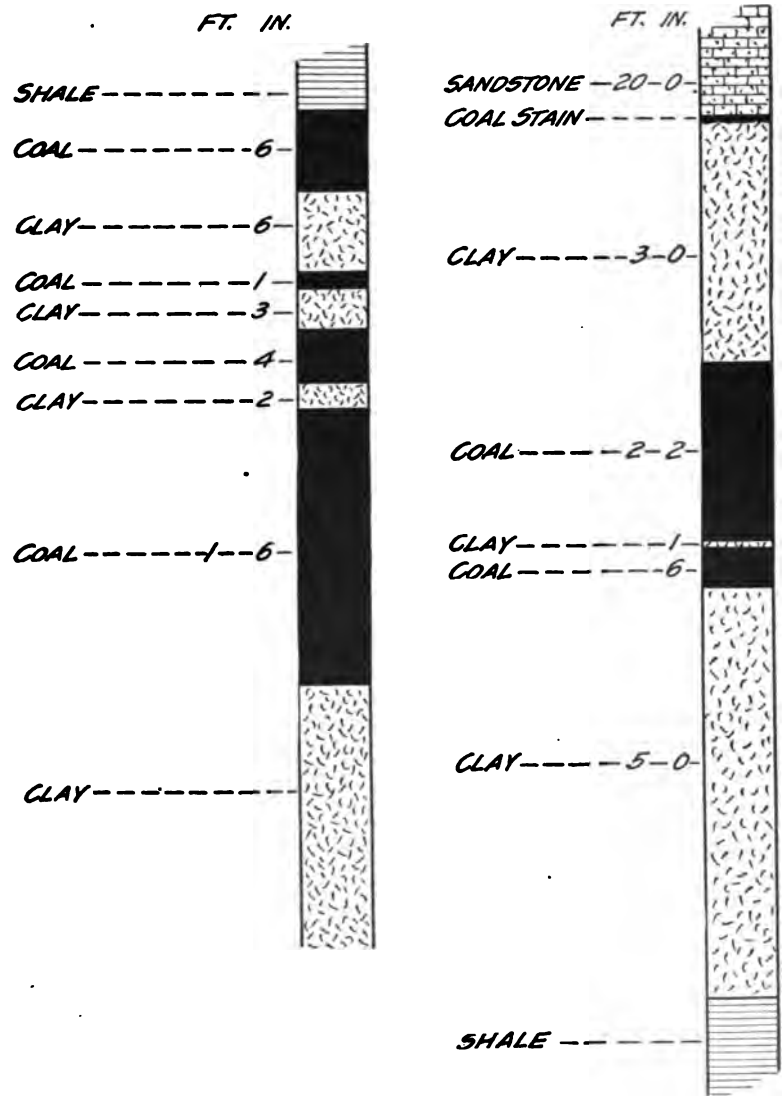
Therefore, the clays were the products formed during the oxidation periods, or when the vegetable matter underwent complete decay. This theory requires no break in the plant life but only in the degree of decomposition or decay.

Some of the relations of clays to coals, found in the Pennsylvania series, are illustrated by the accompanying sections, which were taken in southern Ohio:

Tionesta Coal. Here during the deposition, there was first an oxidation period which formed the bottom clay; then a period in which the vegetable material was preserved; then a period where oxidation again took place, etc., until finally the entire bed was submerged and covered with shale. During the period of formation of coal and clay, there was no break in the plant life but only changes in the conditions during which it changed from periods when the matter was preserved to periods when it was completely oxidized, the probable cause of which was only the rising and falling of the water in the swamp. (See Fig. 1.)

Clay partings in coal deposits are very common. In fact, but few seams, when traced for any considerable distance, are free from them. In some seams, the clay partings are as regular and characteristic as the coal benches themselves. In other seams, although these partings may not be present in the coal strata in the main coal basins, they are of common occurrence in the seams along the borders of the fields where oxidizing conditions are expected. This structure has been observed in the Sharon, Quakertown, Lower Mercer, Upper Mercer, Tionesta, Middle Kittanning, and Lower Freeport coals, and the oxidizing conditions will account for the irregularity of these thin and broken coal benches interbedded with clays. Regular clay partings are characteristic of the Clarion and Lower Kittanning

TRANS. AM. CER. SOC. VOL. XVII. FIG. 1. STOUT



coals and common features in the Middle Kittanning, Upper Freeport and Pittsburg coals.

Bone partings in coal seams also appear to have been produced by the oxidation being carried somewhat beyond the normal during the preserving stage.

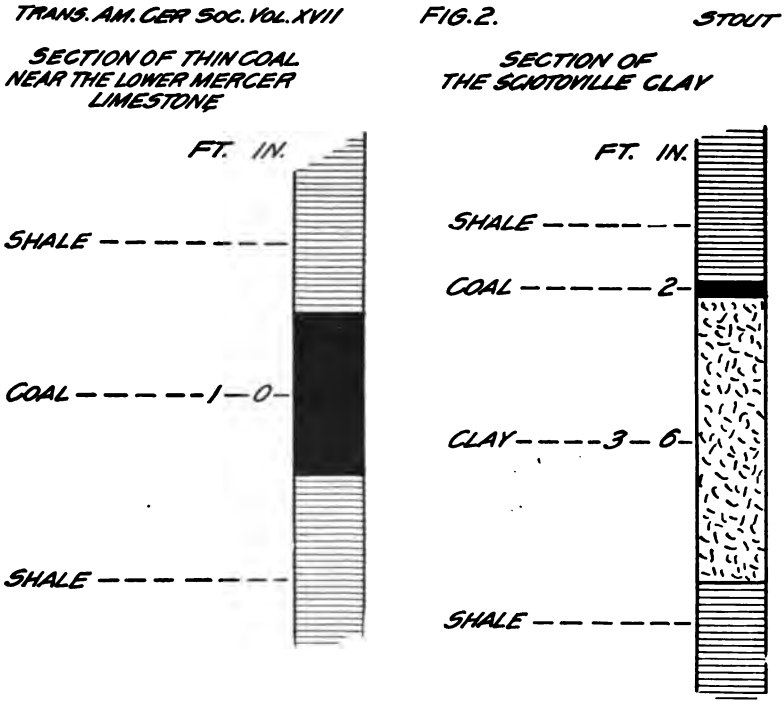
Lower Kittanning Coal. Here, there was a long period of oxidation followed by a short period, where the vegetable matter was preserved; then another short oxidation period followed by a longer period of preservation; then a period of oxidation before final covering by the sands. The clay parting near Etna Station, Lawrence County, Ohio, is only from one-half to one inch in thickness but a true clay, while at Black Fork in the same county, it thickens to two feet and in composition is practically the same as the thick bed below. (See Fig. 1.) The clay above the coal in places is a true flint clay and also differs somewhat in composition. In some localities, this clay lies directly on the coal, but in others the two are separated by from one to thirty feet of shale. The clay really belongs to a different formation.

Mercer Coal. Here there was no period of oxidation of the vegetable matter and consequently no clay beds were laid down. The coal is laid down on a shale and covered by a shale. The shale below shows no effect from the plant life and in no way resembles a clay. (See Fig. 2.)

Sciotoville Clay. Here, the clay was laid down during the oxidation period. The thin coal above represents only the vegetable matter that was buried by the shale, and thus preserved as coal. The deposition of the shale was occasioned by a sinking of the area. Many clay beds show a thin seam or stain above, which may carry for long distances. A point of special interest is the fact that the clay deposits, such as the Sciotoville, Mercer, and Brookville, which are noted for their purity and high aluminous content, seldom have more than an inch or two of coal above them. (See Fig. 2.)

"Pink eye" clays are clays in which the ferric oxide runs from two to fifteen percent or even more. The deposits are found below the flint clay on the Sciotoville clay horizon. They are not persistent but often thicken to several feet. The ferric oxide is

segregated giving the clay a mottled or blotchy appearance. If these clays were originally the muds of swamps purified by plant action, then the iron oxide should be in the ferrous state as this is the form in which it is laid down under such conditions. In the presence of water and decaying organic matter, ferric oxide is reduced to the ferrous state and then by combining with the liberated carbon dioxide should separate as ferrous carbonate if



deposited. Oxidation of the iron could not have taken place after these beds were deposited and covered, for in that case, the iron in the shales below would also be oxidized, which is not the case. The fineness of the iron oxide and the segregation indicate chemical precipitation under oxidizing conditions.

Next, we will consider the character of the clay and of the coal ash, and the relation of the clay and coal deposits.

The analyses of thirteen samples of normal Coal Measures shales gave an average of 60.47 percent kaolinite or its equivalent, and 39.62 percent excess silica. As given before, the analyses of seventy-eight samples of coal and coke ash gave:

73 samples, 85.85 percent kaolinite, 14.17 percent excess silica.
5 samples, 95.87 percent kaolinite, 4.13 percent excess alumina.

While that of forty samples of clay show:

33 samples, 80.48 percent kaolinite, 19.52 percent excess silica.
7 samples, 95.68 percent kaolinite, 4.32 percent excess alumina.

The above analyses show that a clay is not simply a shale with the bases extracted, for in the latter, there is also an excess of silica over and above that in the clay. They show, that to convert a shale sediment into a clay, the plant life must not only remove the greater part of the bases, but it also must remove some silica.

In the formation of a clay, there are three main conditions to consider which are as follows:

(a) That the clays were originally laid down as shale deposits, then plant life growing on these shale soils removed, by direct or indirect action, the greater part of the basic materials and some silica.

(b) That the shale sediments were slowly but more or less continuously deposited throughout the whole swamp period, during which plant life flourished and, through whose action, directly or indirectly, these infiltrating sediments were broken down with loss by solution of bases and silica.

(c) The contribution of clay-like material made by the plant itself; *i. e.*, if the vegetable matter was completely oxidized, was the residual ash a clay-like material?

Let us consider the first condition. The soil-derived elements required by plants are calcium, iron, magnesium, phosphorous, potassium and sulphur. Others commonly present and that may be of use in plant growth are manganese, silica and sodium. Others found under special conditions, though not essential to plant life, as far as known at present, are aluminium, titanium, arsenic, barium and many others in small amounts. It

is a well known fact, that many types of sea weeds are especially high in silica. These mineral constituents are taken up by the plant as soluble compounds.

"It has long been a disputed question to what extent and in what manner the acid solution in the root-hairs helps to dissolve some portion of the soil particles directly. There is good reason to believe that the sap within the root-hairs has some such direct dissolving action on soil particles. The weight of evidence at present appears to indicate that the chief dissolving agent excreted by root-hairs is carbon dioxide, though it is easily conceivable that the acid salts and free organic acids in plant juices may be passed out through the cell wall around the soil particles and take part in the dissolving action."[8]

The common basic elements taken up by the plant then are calcium, iron, magnesium, potassium, sodium, and manganese, while the acid elements are phosphorous and silicon. Under some conditions, alumina is also added to this list.

The extraction of these elements from a shale soil would tend to reduce it to the composition of clay. If the clays were laid down as shales, then through the action of the plant life that grew upon them, and which now is represented by the coal, we would expect a gradual change downward from pure clay at the top of the deposit to shale below. No general gradation is shown, although in some cases a thin, impure substratum is found at the bottom. In many cases, the lower or middle part of the deposit is even more pure than the upper part.

Under this condition also, we should expect, in a general way, to find the purest and thickest clays below the thickest coals. This is not the case but rather the reverse. The very finest clay deposits, such as the Sciotoville of Ohio-Kentucky, and the Mercer and Brookville of Pennsylvania, seldom have more than a few inches of coal above them, while the clays below the Middle Kittanning, Pittsburg or Sharon, even when the coal beds are thick, are seldom of high grade. The clay below the Lower Kittanning coal is usually very good, regardless of whether the coal is thick or thin. The evidence does not favor the assumption that above these pure clays, there were originally heavy deposits of vegetable matter which was largely removed before covered by

[8] Van Slyke—Lucius L., *"Fertilizers and Crops,"* page 166.

the deposits above. In many cases, these thin coals are covered with fine-grained sediments, evidently deposited in quiet waters where the floor materials at most were but little disturbed. These thin coals usually carry for long distances, and the roof shales often contain many well preserved plant fossils, which indicate burial in quiet waters. The shale deposits above them are of the same general character as those above the thick coals. From this view also, the clay below each coal bench should be on the main the work of that particular life zone. A section at the mines of W. R. Maxey, in Lawrence County, Ohio, is as follows:

	feet	*inches*
Sandstone	30	0
Shale	..	4
Coal, shaly	..	5
Coal, good	2	10
Lower Kittanning		
Clay	..	1
Coal	..	9
Clays, lower part siliceous.....	5	6
Clay shale	1	6
Coal, shaly	..	4
Clay, upper part flinty, very good	11	0
Clay shale, with kidney ore	4	0

According to this, if the plant life represented by three feet, seven inches of coal purified the five feet seven inches of clay, the life represented by the four inches of coals should do only about one-eleventh of that amount of work; but below this small stratum, there are eleven feet of clay, and part is of better quality than that above. The nature of the sediments above, and the distance, this thin seam carries, argues against its being originally a thick seam, thinned later by erosion. There is no direct relation between the thickness of the coal and the thickness or the quality of the clay below.

Clays of good quality are often found directly above soft shales. In some cases, they are separated by a parting only, and in most cases, the transition from shale to clay is a matter of a foot or two at most. If the clay beds were originally shale de-

posits purified by the action of plant roots, one would expect this transition to be gradual and long drawn out. In some localities, deposits of high grade clays have a thickness of fifteen or twenty feet or even more. Plant action, sufficient to do the work required, would not reach downward this distance.

In conclusion, with regard to this first view, the relation of clays to coals, as seen in the field, do not favor this origin, especially for the pure clays or for the thicker deposits. This method of purification seems to apply only to some of the thin deposits and to the sub-stratum of some of the thicker beds.

Next, let us consider the second view—that the shale sediments were slowly but more or less continuously deposited throughout the whole swamp period, during which plant life flourished, and through whose action, directly or indirectly, these infiltrating sediments were broken down with loss, by solution, of bases and silica. Here the plant tissue underwent complete decay.

Although some of the important coal seams cover areas of thousands of square miles, most of the deposits are comparatively local. In regard to the areas of coal seams, Stevenson says:[6]

"The areas of individual coal deposits vary from a few square yards to many hundreds of square miles. Those of very limited extent are usually outlying patches, occupying spaces eroded in older rocks, and they abound in some of the western states, where the coal rests unconformably on beds of Mississippian or even greater age. * *

"The query at once presents itself: Are these petty areas exceptional or are they typical? They are from a few yards to several miles in diameter, and we might expect to find yet larger areas, distinctly limited. Are coal beds continuous or do the names applied to them designate only horizons, marking periods when accumulation of coal took place, so to say, contemporaneously at many places and in extensive areas?

"The question has been ra'sed less frequently in Europe than in the United States because the coal fields are of comparatively small extent. But in the bituminous regions of the Appalachian, generalizations presented long ago still hold in the nomenclature, though some observers have opposed them strenuously; * * * * * * * The defective conceptions inherited from the preceding generation were

[6] Stevenson—John J., *"Formations of Coal Beds,"* pp. 379, 382-385.

accepted and continuity of coal beds was taken as the fact, barren areas being regarded as exceptional. This belief was strengthened by the known distribution of the Pittsburg coal bed, which appeared to have been proven within an area of not far from 15,000 square miles. But the multitude of shafts, the vast number of oil-well records, the increased number of natural exposures, due to railway and road construction, have provided data during the last twenty-five years, which compel modification of opinion. * * * * * * * * * * * * *

"The Pittsburg, Waynesburg and Washington, in the upper portion of the series, approach as nearly to continuity as one may conceive, for they are always present in exposures and records within an area of thousands of square miles; but the Pittsburg shows remarkable variation in thickness; it thins away to nothing from all sides towards the central part of the area, while at times only its underclay remains to mark the horizon. The Waynesburg and Washington horizons are persistent, coal or black shale being present, but there is often only a trace of coal, while the variations in structure of the deposits are extreme. Some Conemaugh coals are practically continuous, according to natural exposures, in Ohio within an area of not far from one thousand square miles, but they are rarely seen in Pennsylvania; others are present on the east side of the region and rarely appear on the west side. The Allegheny conditions are similar; on bed attains great commercial importance within an area of perhaps a thousand square miles in Ohio, but in Pennsylvania and West Virginia, it is only occasionally important, and it is practically wanting in considerable areas. And the statement is true of other coal horizons. The evidence goes to show that there were periods, longer or shorter, during which proper conditions existed, so to say, contemporaneously, in many localities, but did not exist in very many others. The greatest unbroken area, after the close of the Pottsville, in which coal accumulated, was that at the Pittsburg horizon, the coal having been proved up in an area of approximately eight thousand square miles. Originally it was greater, for erosion has removed much. * * * *

"Accepting, however, the extreme conceived area for original extent of the Sewanee or the Pittsburg, one is compelled to recognize that accumulation of coal was not in progress at any time in an area of more than thirty thousand square miles and that it never was in progress simultaneously in all parts of that area; that at most, horizon conditions were favorable to accumulation in areas of a few square miles to some hundreds of square miles, while in perhaps the greater part of the regions the conditions were unfavorable. In fine, that the conditions were very much like those existing today. And this has always been the case. * * * * * * At all periods, conditions favorable to accumulation of coal have existed in comparatively small areas, more or less widely scattered."

As shown from the above, while some of the coals extend over a large area, most of the seams are comparatively local in extent. Many coals are really a collection of more or less isolated pockets.

In any particular stratum, there are usually many wants. Some of these indicate regions that were above water, or land areas at the time the coal was being laid down, for along the border of the deposit, the stratum goes out in sandstone as finger coal, indicating shore or delta action. Along the border of other wants, the stratum is seen to break up into thin layers with shales intervening, and finally goes out completely, indicating deeper water action. The shale sediments were brought in by current action. These conditions are quite common, especially with the coals in the Allegheney and Pottsville formations of Ohio. Thus, the structure of the coal strata point to local land areas and to more or less current action along restricted lines in the coal swamps.

The great coal basins were partially or completely separated by anticlines and mountain ranges, while each particular stratum was restricted to more local areas. In a general way, these land areas were favorably situated for producing sediments, for the coals constitute only a small fraction of the total coal measure rocks. The supply of sediments evidently was abundant.

As given above, the manner in which some coal strata go out indicate mild current action. Some circulation of water is necessary for a thrifty growth of plant life, for if the water in a basin becomes very acid, the plants die. Many of the smaller swamps were probably subjected to flood periods causing a circulation of the waters.

The main points in the above are:

(a) That the coal basins with few exceptions were comparatively small.

(b) That the land areas were able to supply a large amount of sediment.

(c) That there was some circulation in the coal swamps.

Therefore, there was some clastic sediment deposited more or less continuously during the whole swamp period.

Next consider the effects of plant life on these slowly but more or less continuously deposited clastic sediments, and the resultant products produced when the organic matter underwent complete decay and solution action occurred. As has been previously stated, the action of the plant is to take up as common constituents, calcium, phosphorous, potassium, magnesium, iron and silicon. Others taken up in smaller amounts are sodium, aluminium, and titanium.

Calcium, magnesium, iron, potassium and sodium constitute the main basic impurities in clays, while phosphorous and titanium are two common acid impurities.

The mineral ingredients are taken up by the root-hairs of the plants as soluble compounds. Some of the mineral matter is deposited in the solid constituents of the plant, but part remains in the sap fluids. The flora in these coal basins evidently varied like that seen today in swamps; *i. e.*, from floating algae to arboreal types.

White says:[7] "The examination of coal shows that the kinds of ingredient plants range all the way from algae and fungi to large trees of various orders."

Infiltrating sediments would in part be entrapped by various floating types; that sediment which settles would be entrapped by the root-hairs of the smaller types of life growing on the bottom. Even the large arboreal types throw out many surface roots. The result would be the extraction of a part, at least, of the mineral elements necessary for plant life from these sediments. If the deposits were slowly built up during oxidizing conditions, these sediments would be subjected to this action for considerable periods. They would thus be subjected to the action of all types of life in the swamp, as they went through the cycle from surface sediments to those deeply buried.

This action means the breaking down and extraction of bases and probably silica from the feldspars, micas, amphiboles, pyroxenes, olivines and others types of minerals. During this breaking down, due to the complete chemical rearrangement, the

[7] White—David, *Bull. 38, Bureau of Mines*, page 1.

silica would be in a condition favorable for solution and thus plant assimilation. This type of silica would evidently be more easily attacked than that in the form of the very insoluble quartz. One of the principal residual products of the weathering of such minerals is kaolinite. We should expect the same with the breaking up of these, due to plant life. The extraction of such bases and acids found in the plants from normal clastic sediments will leave a product approaching in composition that of normal clays.

Under oxidizing conditions in these swamps, the plant life undergoes complete decay. A part of this assimilated mineral matter would remain as a precipitate or residue, a part also, especially that in the sap-fluids, would go into solution in the swamp waters, and through swamp circulation or during flood periods this would be removed from the field of action. It is known that there are many soluble organic compounds of silicon, some of which occur in plants, so this component may also be lost through plant action. During decay of plant life in presence of moisture or water, soluble compounds are also produced. Lime, magnesia and ferrous oxide form soluble bi-carbonates. Most sodium and potassium salts are soluble, while phosphorous forms a number of soluble compounds. Some circulation and change of water is necessary in the swamps, for plant life will not thrive in very acid waters; and if there were no plant life, the sediments would be normal clastic deposits and not clays. This continued action, under the conditions outlined above, would thus slowly but gradually eliminate many elements from the original sediments and reduce them to clay-like bodies.

Under these conditions, the character of the resultant deposits would depend on the following:

(a) On the character of the clastic sediment; *i. e.*, whether a fine shaly sediment or a coarse sandy one.

(b) On the rate of deposition. The slower the deposition, other things being equal, the more complete the transformation from clastic sediment to clay.

(c) On the amount of the direct and indirect plant action. The greater the amount of such action, the more complete the elimination of basic and acid impurities.

The general conclusion here is that the shale sediments, which were slowly, but more or less continuously, deposited throughout the whole swamp period, during which plant life flourished, and through whose action, directly or indirectly, the sediments were broken down with the loss by solution of bases and silica, and were thus converted to clays.

The next point is, what part did the ash of the plant itself contribute to the clays? Speaking of the ashes or inorganic ingredients of coal, Thiessen says:[8]

"Although during the investigation here reported, no special attention was paid to inorganic ingredients, yet a few observations were made, and here and there certain phenomena came to notice.

"The visible inorganic constituents occur as calcium compounds in fissures or cracks, as a silicon compound between certain laminae or in the canals of silicified wood particles, and as pyrites either in cracks or fissures, as calcium deposits, or as minute spherules imbedded in the laminae.

"Both the calcium and the pyrites deposits may be a millimeter or more thick, but most of them are extremely thin. The calcium has usually been deposited in fractures of the coal; *i. e.*, in actual breaks of comparatively recent age, made after the coal had assumed its present conditions. The fractures, though they may run in any conceivable direction, run most frequently in a horizontal and in a perpendicular direction, more or less at right angles to each other. Pyrite is deposited in the same way, but may also occur in any part of a coal in the form, usually, of nodules and granules. As far as observations were made, siliceous deposits do not occur in this fashion, but as horizontal, thin, irregular deposits between the laminae or sheets, and in silicified fragments of wood, and originated in earlier times or during the formation of the coal. But these visible ingredients do not comprise all the mineral matter in the coal; in fact, they comprise only a small part, because when a fragment of coal in which no minerals are visible is burned carefully, inorganic components are left uniformly over the whole fragment, the original form and texture of which is retained. The inorganic substances are seemingly in chemical union or close association with the organic components of the coal; this we know to be possible from the chemistry of the organic products."

As has been shown from the analyses of the seventy-eight samples of coal and coke ash, this mineral residue is highly

[8] Thiessen—Rheinhardt, *Bull. 38, Bureau of Mines*, page 266.

aluminous, even more so than ordinary clays. In the ash of some of the so-called pure coals, the alumina is even above that in pure kaolinite; it agrees closely with the amount found in the high aluminous clays, such as are found at Olive Hill, Ky., and elsewhere. In these pure coals, the clastic sediments are practically wanting, or low, or the preserved plants left no mineral residue and the former conditions seem the most natural.

"Mietzsch points out that living Lycopodiaceae contain from twenty-two to twenty-six percent of clayey earth in the ash and asks why one should suppose that the older types were different. But if the coal contains an abnormal proportion of ash, there is reason to recognize influx of fine mud."[9]

The silica and alumina may have been assimilated in amounts somewhat similar to that found in the mineral kaolinite, or if the silica was taken up in excess of this, during the maceration process, this component and alumina may have combined, in part at least, with renewal of the main excess of silica by solution. If combination took place, and the conditions thus favor ease of chemical action, kaolinite would be the compound expected.

Summary. In review of the above, the evidence favors strongly the assumption that the plant residue was a clay-like body, highly aluminous, and resembled the so-called pure clays in composition and in texture.

Such being the case, under continued oxidizing conditions, the residual products of the plant life would build up a clay deposit. This will account for the remarkable physical properties, such as the colloidal character, homogeneity, and freedom from impurities. and for the constancy of relation of the silica, alumina and water of clays. It seems evident that in the pure clays, the plant ash was the predominating or at least one of the important factors.

In review of the whole subject some of the important points are as follows:

(a) No break in the plant life is required during deposition of clay and coal, only a change from oxidizing to preserving conditions.

[9] Stevenson—John J., *"Formation of Coal Beds,"* page 49.

(b) This origin of clays seems the natural and easy way of explaining the cause of the clay partings found in coal strata.

(c) It accounts for the constancy of relation of clay and coal.

(d) The gradual building up of clay deposits gives a cause for the varieties of clays. In the pure clays, the plant ash is considered an important, if not the predominating factor. In the intermediate varieties, the character of a clay in a general way depends on the rate of deposition and character of the clastic sediments, on the extent of the direct and indirect action of the plant life, and on the residue contributed by the decayed organic matter. The character of the impure clays of sub-strata depends primarily on root action only.

(e) Repetition of similar conditions, evidently in force during the preservation of the different coals accounts for the occurrence of pure clays on different horizons. Due to persistency of conditions, clays, like coals, may be similar in composition over wide areas.

(f) This origin explains the important chemical and physical properties of these clays.

(g) The clays account for a part at least of the oxidized plant life that flourished during coal measure time. In a general way, the clays are a measure of the amount of plant life.

This view of the origin of clays fits the facts as observed in the field.

DISCUSSION

Prof. Binns: I have listened with unusual pleasure to this presentation. Like others, I suppose I have offered the theory, not first hand by any means, that the fire clay forms the bed in which the coal products grew, and so forth. I have alluded to that a great many times in classes, but I was all the time apologizing to myself because it did not seem entirely satisfactory. Now this theory is presented, and at first thought it seems to me most attractive. I would like to ask the speaker a question with reference to the kind of clay to which he alluded. As far as my

study of it has gone, the deposit has always seemed to present a gradual change from the clay substance to the rock above.

Mr. Stout: The Clarion deposits, as I saw it in Thomas's mines, do not show that gradation. I analyzed the clay from two of his mines. In one, the deposit was seventeen feet in thickness, and the clay was all flint of practically the same grade; in fact, it stood cone 35. The analysis runs something like 46 or 47 percent silica with about 38 percent aluminum. In the second mine there is a plastic clay above, which he does not take down. There is a coal strain, as I recall it, about an inch or two in thickness above the flint clay, and another above the plastic clay. In the second mine there is no plastic clay above, for the roof is sandstone.

Prof. Binns: Perhaps we are speaking of two different things. I was not alluding to the Ohio clays but the Clarion deposit, as it appears in Pennsylvania.

Mr. Stout: These mines are located near Lucinda, in Clarion County, Pa.

Mr. Hice: Is it Clarion or Mercer?

Mr. Stout: It is Mercer.

Prof. Binns: I was speaking of the clay called Clarion clay in Pennsylvania, and not the Mercer clay.

Mr. Stout: Mr. Thomas calls it Clarion clay as it is from Clarion County. It is not in the Clarion group, but in the Mercer below.

Prof. Binns: I had occasion to investigate a deposit of Clarion clay in Pennsylvania, in the middle of a railroad tunnel, and the tunnel passed clear through the clay. The clay merged into a rock above without any trace of coal blossom between.

Prof. Orton: I want to say that for anyone who has attempted to teach the origin of clays, as I have for a good many years past, this theory of Mr. Stout's clears up a great many things which have been annoying, because contradictory or obscure. I remember very well when he first told me of his idea, and at that time he had not elaborated it to nearly its present extent, but it seemed at that time to cast a powerful searchlight

into what has always been one of the least convincing phases of stratigraphic geology.

In accounting for the origin of clays, we have a number of very different formations to consider. The rotting of the old feldsphatic rocks in the formation of primary kaolinite clays is, of course, the typical illustration that has always been given as the source of our clays, and we all know where such formations are to be seen; but, the formation of a typical primary clay by weathering does not help most of us to recognize that such a clay has anything in common with the kind of clays we have to deal with. Common clays of all ordinary types are so far removed from the primary clay, that we cannot see any necessary connection or casual relation of the one to the other. We find great masses of clay which have evidently been brought together as the product of recent glacial action. We find another big group of clays which consist of sediments being moved by erosion from the mountain highlands to the ocean depths and which form, while resting temporarily on their journey, the alluvial river beds and flood-plain clays. These three groups of clays are of vast mass and relatively simple origin and can be understood and rationally classified.

But when we come to the clay beds, which are interstratified all through the coal measure formations, we have a set of deposits which do not resemble very closely any of the four types that have been mentioned neither primary clays or shales or glacial clays or alluvial clay, though they vary greatly in character and many of them are not especially fire-resisting and occur almost always in connection with coal beds either under the coal or taking the place of the coal, and sometimes interlarded through the coal, or actually on top of it. The old theory has been that the clay represents the soil, from which the coal forest grew, and its difference from other soils is due to the purifying action of vegetable life, which absorbed its alkali and silica and left the aluminous residue. This theory that the coal-measure fire clays are the soils of the coal forests modified by the selective absorption of centuries of vigorous plant growth has always seemed inconsistent. If the soil bed, on which the coal swamp

grew, had been leached through centuries of plant activitiy, you should find some differences between the upper layers and the lower layers of it. If the soil was originally an ordinary marine sediment like a shale, and the vegetation has been exhausting it for a long time, then naturally, it would be less exhausted in its deepest layers to which the roots did not penetrate much, and more exhausted at the top. We see plenty of illustrations in the swamps which have formed during glacial times. Their soil is less and less affected as you go down deeper from the surface, and shortly you get to where it is not affected at all. That is what we should expect to find, if this soil exhaustion theory for the coal-measure fire clays were true. But it doesn't usually come so. As Prof. Binns has aptly said, I have always felt like apologizing in trying to explain this theory to students, because it never did ring quite true.

Mr. Stout has boldly taken this mass of discordant facts, and, by turning the hypothesis wrong end foremost, has given us a theory which harmonizes all these discords and gives a logical and simple explanation for the variations which the coal-measure fire clays show, both in composition and stratigraphic arrangement. He assumes that these clays which always burn buff, except when impregnated with clearly extraneous or accessory minerals, are the mineral matter taken from the soil of the coal forest by the roots of the trees, and which constitute the ash or mineral residue when the organic tissue has been oxidized and gone back into carbon dioxide and water. If the forest grew just above the water level, oxidation would get rid of all the carbonaceous matter, and leave only the mineral matter behind. If the forest were just on the water level, or the water was fluctuating up and down a little, then mineral matter with or without carbon would be formed, according as the water covered or did not cover the decaying forest products. If the water were persistently high, then carbon and ash would be going down on the bottom in a black sludge. The theory seems to explain all ratios of ash and carbon from clear clay with no carbon in it up to practically clear carbon with only a percent or two of ash as the limit.

It likewise accounts for the facts of stratification of clay and coal in every possible sequence. We cannot explain very well by the old theory, why a coal may have its clay over it or mixed through it in bands instead of below it. By the Stout theory, one order is as logical as another. Accumulation under oxidizing conditions gives clay. Under reducing conditions, where water cuts off free oxidation, we get coal. Under alternating conditions we get streaks of clay in coal or streaks of coal in clay, both of which are commonly seen.

Likewise, by intermixture of the ash from vegetation and clay sediments brought in by muddy water, we can see how every gradation from pure buff-burning ash to clay with no appreciable ash in it would be formed in the normal variations of swamp growth. Fire clays which vary sharply in the silica-alumina ratio and in color in their adjacent laminae are explained by the Stout hypothesis, and very puzzling by the old theory.

The satisfactoriness of a theory is tested by its ability to explain large masses of otherwise discordant facts. Stout's theory does this. With no other basis, I think it would win ultimate acceptance. But when the close relation between fire clays and the ash of many different coals is shown, a powerful additional argument is furnished.

It was my good fortune to spend part of one day last summer in the mines and clay works at Hoganas in Sweden. This plant is owned by the largest company of the sort in Sweden, who own practically all of the coal measure formation in that part of the kingdom. This plant affords a fine variety of minerals illustrating just the theory that Mr. Stout has expounded. They are mining clays and coals which are mixtures of carbon and clay in almost every proportion. The coals run from as low as 50 percent carbon and 50 percent ash on up to 85 percent carbon and 15 percent ash. The clays run from 50 percent carbon and 50 percent clay to practically pure clay and no carbon. They are actually taking out coal from their pit containing about 50 percent combustible and 50 percent ash and putting it into gas generators and converting the carbon into producer gas,

and then taking the residual mineral matter from the producers grinding it up, mixing it with a little fresh plastic material and making it into high grade refractory fire-bricks. These ash bricks have the same silica-alumina ratio that we find in good fire clays.

The Hoganas works illustrates better than any American clay works, of which I have knowledge, the close and intimate relationship between the actual substance of coal and clay, which Mr. Stout's theory essays to explain. In my opinion, he has made a memorable contribution to the subject and has brought the origin of the most obscure and baffling group of clays into as clear and comprehensible a state as exists for the shales, glacial clays, and alluvial deposits.

Prof. Binns: Prof. Orton spoke of the fire clays as stratified. But there is a peculiar appearance of these clays on cleavage, which is commonly known as "slickensided," and which I have never been able to account for. Mr. Stout did not commit himself on that, but I would like to hear him. I have never seen slickensided structure and stratification in the same clay.

Mr. Stout: Slickensides in clays is evidently formed by pressure during the time when they were rather plastic; it is simply pressure slips; you will find it not only in clays, but in the calcareous shales. The example I have in mind is a shale between two limestone beds which contains 56 percent calcium carbonate and has numerous pressure slips. Also in one of the blue hard limestone deposits in the coal measures, there are pressure slips, evidently formed when the mass was in a plastic condition. I would like to answer the remark made by Mr. Binns about the clay grading into the sandstone above. The sandstone, as you know, were deposited by currents, which in many cases modified the beds below or partially replaced them. The division between beds are often not sharp, for the type and character of deposits depend on the velocity of the currents which were continually changing.

Mr. Longnecker: I would like to ask Mr. Stout a few questions with the idea of bringing out a little further information. One is how he explains the formation of nodule clays, particu-

larly in the Pennsylvania district, and at the same time why the hard clays—I suppose they are brought about by the same formation—are generally more refractory and purer than soft clays?

Mr. Stout: There is a slight difference between the flint and semi-flint clays, but if you take the analysis of flints, semi-flints and plastic clays of Olive Hill, Ky., I doubt very much if you can pick them out. Nodules are of secondary origin; they grew after the beds were laid down. They might have a slight action on the clay for in some of the Pennsylvania clays you will find nodules of practically pure silica.

Mr. Longnecker: How do you explain the sulphur in those clays?

Mr. Stout: In most of these clays, you will find the sulphur as pyrite or marcasite. Iron sulphide will start to nodulize around a bit of carbon or any small grain that may start a crystalline growth. These nodules are of secondary origin.

Mr. Hice: I want to say that I am much interested in the talk. I heard somewhere a rumor of the thing, before I heard Prof. Orton talk about it, but I cannot altogether agree with the statement in regard to the uniformity of the fireclays. While it is not universally, it is very commonly the case in western Pennsylvania, that the top of our fire clays is of very much better quality than the lower portion, less sandy and recognized as being better by everyone. Now that applies in many places to Clarion clay, it applies to the Kittanning clays, it applies to lower Freeport clays. While it is not universally the case, it is exceedingly common, and exactly in harmony with the old idea, but while that is so, I am free to confess that I would like to have the paper itself because I have some matters coming up in which I certainly would like to borrow a lot of the ideas.

Mr. Stout: The great mass of the clays, of course, are not extremely pure. If we get a pure clay, we can easily dilute it. If we have sediments or shale matter coming in there at a rapid rate, the plant would not be able to change all of it. The char-

acter of the clay will depend upon the rate of sedimentation and on the intensity of the plant action.

Prof. Orton: It is not possible by any artificial process of introducing iron into a white-burning primary kaolin to make it give anything resembling the buff or yellow color which the coal-measure fire clays generate on burning. If the old theory of the descent of clay from kaolinite be true, and all clays have been in one way or other formed from the dilution of concentration of such kaolinite matter, we are constantly troubled to account for the characteristic and uniform color behavior of the group we find associated with coal formation. On the other hand, if these clay formations have not come from kaolinite at all, but are really the ashes of many generations of plants, mixed more or less with extraneous or accessory minerals which have been washed into swamps where the plants were growing, by flood water and also with chemical precipitates of carbonate of calcium, iron pyrites and other similar materials, the color character is easier to comprehend. The ease with which iron pyrites will filtrate into any kind of mineral matrix and makes its home there is well known. I once got hold of a sample of clay from the Philippine Islands, evidently of recent superficial formation, full of plant remains and half decayed vegetation, and yet containing pyrites in great abundance. It was possible by putting the clay in slip form through a series of sieves to catch on each sieve, a crop of beautifully formed and perfect crystals, the coarsest being about twenty mesh and the finest microscopic. These pyrites crystals had grown in that clay in the swamp where it formed in very recent time. If pyrites can grow under such conditions as obtain in the present superficial clay beds of the Philippines, I cannot imagine that there would be any difficulty in accounting for the infiltration of pyrites in the sediments forming in the swamps of the Carboniferous Period. In the same way, the presence of white-cap carbonate of lime, and gypsum and practically all the other minerals which are the cause of irregularity of composition of the ordinary fire clay and the ordinary coal ash can be explained. Subtract them as Mr. Stout has done from the clay or ash and compute the ratios of the

residual matter, and you will find that produces the general ratios of kaolinite or mixtures of kaolinite with free silica.

Mr. Lovejoy: I would like to ask Prof. Orton to take an average shale, remove the iron and perhaps some of the alkali, and how far will it differ from the analysis of our No. 2 fire clay?

Prof. Orton: It differs from an ordinary No. 2 fireclay in having probably six to eight percent more alumina and a corresponding diminution in silica.

Mr. Lovejoy: That is, the fire clay is higher in alumina?

Prof. Orton: Yes, it averages higher.

Mr. Lovejoy: The fire clays at Union Furnace ran around the neighborhood of 68 percent silica.

Prof. Orton: That is an unusually siliceous one.

Mr. Lovejoy: I think you will find at the lower Kittanning, they run quite as siliceous as that, one to three feet of fairly good clay in the upper part, and in the lower part six, seven or eight feet is very siliceous, running into almost sand rock. They occur in three somewhat distinct beds, not distinct to the extent of a division between the coal and the clay, but sufficiently distinct, so that any one of these levels makes a good shoveling floor. Now the lower part of the bed at Darlington, I remember particularly, is very sandy. Union Furnace clay is sandy all the way through. The upper part of No. 4, at Shawnee, as I remember, is fairly plastic. I agree with Mr. Hice in regard to changes from good clay into sandy clay, I think that is the rule rather than the exception. In the Olive Hill district, I remember in one mine there particularly, they leave large sections of the flint clay, because it is so highly impregnated with the sulphide of iron, which is so fine that one cannot see it with the naked eye. The only way they can distinguish it, is to take samples of it and burn it in the furnace, and if it burns red or brown, they reject it. They do not always reject it, because I have seen great masses which burned dark brown, evidently containing five or six percent of iron. It seems to me that possibly our No. 2 fire clays

have been affected by the swamp growth. The vegetable matter in its decay developed humus acid in a high degree which worked through these beds below, carrying away, perhaps, some silica, carrying away iron, perhaps, and some of the alkalies, but whenever it struck a bed into which it could not permeate, the solution would flow off on the level, and this makes our distinction between the soft clays and the harder beds below; in other words, the different clays, as Mr. Hice has suggested. I have never given the matter very deep thought, but this idea of Mr. Stout is an entirely new one, and there are a good many points in it that need to be cleared up, which no doubt he can clear up as he studies it more, but I think he has his life work ahead of him.

Prof. Orton: Mr. Lovejoy asked me a minute ago the difference in the alumina content of the ordinary shales and the ordinary fire clays. I recall a table of analyses I collected for the Geological Survey of Ohio, Vol. VII, containing perhaps a dozen or fifteen shales and a similar number of No. 2 fire clays, such as I found being used for stoneware or sewerpipe. The average alumina in the shale group was about 18 percent and the average alumina in the fire clay group was 24 to 26 percent. I think these are fairly representative figures. Of course, it is very easy to pick out individual illustrations of both shales and fire clays which will vary from these proportions and even change places, but I don't believe that anyone will seriously question the statement, that the average coal measure fire clays are notably higher in alumina than the average coal measure shale with which they are interstratified.

Mr. Lovejoy: I cannot conceive of any acid from vegetable matter carrying away soluble silica, which would easily explain the lower silica content or higher alumina content in the fireclay.

Mr. Stout: If you have low aluminous sediments being carried into these swamps, you would naturally expect siliceous clays. Much of the iron in the Olive Hill clay, you will find is in the form of crystals of pyrite or mascasite. Close examination with a glass shows that in the blotchy clay, the particles are very small. Where the plant roots show in the clay, you will find

very thin scales of pyrite. The iron in the upper part of the bed occurs principally as pyrite.

Mr. Lovejoy: We shipped quite a quantity of the Olive Hill clay quite a good many years ago and finally rejected it, because it ran too high in iron; the iron was not in the form of crystals but little round pinheads. In Hotten County, we started to use one clay and did use some of it but finally rejected it, because it gave us excessive trouble with efflorescence. I found upon examination, that the trouble with this clay was that it was highly impregnated with these minute concretions of sulphide of iron and not crystals. I don't recall that I ever found any crystals in that clay, but I have frequently found crystals in other clays. While I cannot imagine how it could come to pass, I have often wondered whether the sulphide of iron, we found in those clays, instead of being infiltrated into the clays, was not a concentration or segregation of the iron of the clay in the form of a concretion, and in that way, concentrating the iron and giving us the clay surrounding it. I know that when you take some of these clays from Olive Hill and burn them, you get fully the dark brown color you get from any of our shales.

DISCUSSION SUBMITTED AFTER THE READING OF THE PAPER

Mr. Longnecker: Since hearing Mr. Stout's theory of the formation of our fire clays, I have noted the similarity in chemical composition of some coal ashes, of which I happen to have analyses. These ashes resemble fire clays in their composition and roughly conform to fire clay specifications (Vol. VII, Bureau of Standards) as regards R O content and the Al_2O_3—SiO_2 ratio. This suggests the possibility of manufacturing a No. 2 fire brick from coal ashes—using the dry-press process. I believe that brick could be made from this material.

The analyses of the coal ashes are as follows:

TABLE—NEW YORK COALS

COALS	ASH ANALYSES			TEMPERATURE OF FUSION OF ASH
Rockhill.....	.0826 CaO .1465 Fe_2O_3	} 1 Al_2O_3 . 1.76 SiO_2		2797°F
	.2291 RO			
Forge.....	.077 CaO .25 Fe_2O_3	} 1 Al_2O_3 . 2.04 SiO_2		2782°F
	.327			
Queen..... Mahoning.....	.0566 CaO .185 Fe_2O_3	} 1 Al_2O_3 . 1.68 SiO_2		2866°F
	.2416			
United.....	.035 MgO .068 CaO .083 Fe_2O_3	} 1 Al_2O_3 . 1.835 SiO_2		2607°F
	.186			
Davis Special.	.0436 MgO .104 CaO .392 Fe_2O_3	} 1 Al_2O_3 . 2.13 SiO_2		2409°F
	.5396			
Blain.....	.101 CaO .337 Fe_2O_3	} 1 Al_2O_3 . 1.93 SiO_2		2525°F
	.438			
Matie Ridge..	.456 CaO .091 Fe_2O_3	} 1 Al_2O_3 . 2.395 SiO_2		2100°F
	.547			

NOTES ON GERMAN CLAYWORKING PLANTS

BY T. W. GARVE

In 1913, it was my pleasure to get admission into several German clay working plants. Clayworkers are dealing with the same problems and have the same difficulties all over the world.

In this country, clayworkers help each other by exchanging ideas freely and by visiting each other's plants, but in Germany the clayworkers are very exclusive and guard their factories with sedulous care, and yet in their conventions they discuss their problems and solutions quite as freely as we do in America. It is not that the Germans are more secretive than we, but the difference is due to the prevailing conditions. In Germany, the markets are very largely local, and competition is keen. In this country the several markets draw their product, even common bricks, from a much wider territory.

Probably face-brick manufacture in America has large influence in keeping the factories open to inspection of competitors. Germany is not a large producer of face bricks, while America leads the world in this respect, and in this product, distance is not considered. A hundred miles is only a local haul. Five hundred miles is the natural territory of many factories, and hauls of one and two thousand miles are of too common occurrence to be worthy of comment.

The first brick plant, which I will describe, is in the outskirts of Leipzig and turns out between 50,000 and 100,000 bricks daily, being the largest in that vicinity. It is making a very good common brick, using an old river (alluvial) deposit. The clay pit is situated in the woods about a mile from the plant. There was no steam shovel or clay digger in evidence, but instead, there were ten men working in the pit shoveling the clay into cars which were hauled to the plant by a small locomotive, ten cars at a time. The plant is situated on the main highway and is completely enclosed by an iron fence on a brick wall base with a stone coping. In one form or another such attractive enclosures are characteristic of German plants.

The train of clay cars enters from the main highway through a large gate and is stopped alongside of a continuous kiln.

An electric overhead mono-rail traveling crane picks up the box of each car, moves it forward and around a curve across the end of the kiln to the factory on the other side where the load is automatically above a large disc feeder. From the feeder, the clay passes by gravity through two sets of rolls to the brick machine. About four feet in front of the die of the machine is the cutter, operated by one man. The cutters almost exclusively used in Germany consist of a base or frame with a small carriage,

FIG. 1

on top of which a swinging arm with two or three cutting wires is attached. The carriage has a little upright board at its end by which the end of the clay bar pushes out the carriage while the man is swinging down the arm or wire holder to cut the end of the bar into bricks, which is done without waste. These cutters are also built for automatic operation. In this factory three bricks were being cut at each stroke, and one man hacked them on a car, handling 50,000 bricks per day of eleven hours.

The German sized brick has 120 cubic inches, while our brick has only 74.25 cubic inches. Taking the working day of

ten hours, which is the rule in this country, we have a capacity of 45,500 German bricks or 73,500 American bricks from cutter to car per man.

This is accomplished by the relative positions of the car, take-off and cutter, being such that the take-off has only to make

FIG. 2

a quarter turn from the cutter to the car, but it must be mentioned that the bricks are not separated on the cars. This work is done by boys or women after the bricks are finally placed in the drying racks.

There were two continuous kilns, but the drying was done only on top of one kiln and in sheds distributed over a large area round the plant. An immense number of drying racks must be available, since the drying proceeds very slowly; it takes several weeks in the outside racks and perhaps five to ten days in the kiln racks. Leipzig is situated very low, and the atmosphere is frequently damp. Usually there are about two million bricks in the drying racks.

One of the continuous kilns is of the Hoffman type and one of the Dannenberg type, both "*ringofens*," and it takes about

FIG. 3

eleven days to make a complete round of a kiln. They use nut brown-coal and pulverized brown-coal of the same quality, for which they pay M 13.40 or $3.30 per ton for the former and M 8.40 or $2.00 per ton for the latter. The fuel for burning and power figured M 3.00 or $0.71 per thousand bricks (German size).

There were no bricks shipped by railroad. All were hauled to the city and over the neighboring country by big auto trucks,

with trailers, the roads being in perfect condition. The market price of the bricks was between M 22 and M 24, or $5.50 to $6.00 per thousand.

Figure 1 shows a brick plant in Berka, a small town of Thuringia, as seen from the clay bank. This plant is making common brick and hollow floor blocks chiefly for the country trade.

The clay in the nearby pit is of the most irregular character. There are streaks and pockets of lime and limey clay mixed with outcrops of fat as well as lean clay. Lime is the greatest enemy

FIG. 4

of this factory, and the men in the clay pit have to sort out as much of the lime and limey clay as possible. There are three pick-men in the pit, and upon them the quality of the product chiefly depends.

The cars are pulled up, on an incline, one at a time, by a belt-driven winding drum, and the clay is dumped into a large cylinder above a rotary disc feeder. The clay is always wet, and to insure proper feeding a set of curved arms above the disc rotates with it and helps to push out the clay through the side

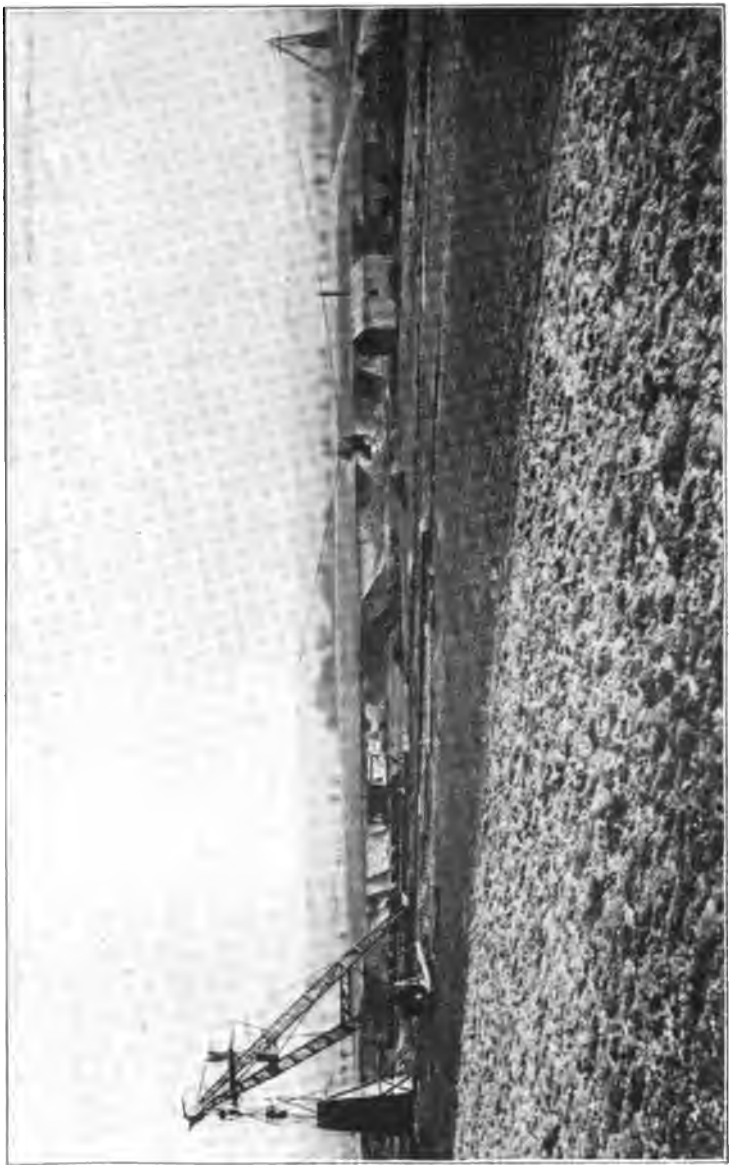


FIG. 5

opening along the scraper. The disc is of large diameter and is resting on little rólls.

In its downward path, the clay first passes a set of toothed rolls which have a speed of about 100 r.p.m., and then through a set of rolls of 22 inch and 26 inch diameters, and 24 inches long. They rotate 100 to 120 revolutions per minute and have a side motion for grinding effect on the clay. Finally the clay passes a set of smooth feeding rolls and then enters the auger brick machine. In Figure 2, we see this line of machinery from the toothed rolls to the brick machine. Fine grinding is one of the methods of overcoming the difficulties with limey clays.

The lime burns to caustic lime which, when exposed to atmospheric moisture slakes and swells and in swelling bursts off flakes of the brick, called in this country "popping." But when the grains are very small and thoroughly distributed, the increase in volume through slaking simply fills, more or less, the pore spaces in the bricks without causing rupture.

The cutter is similar to the one described previously, but here only two bricks are cut at a time. (Refer to Fig. 2). The take-off at the end of the cutter places the bricks, two at a time, upon the trays of a tray elevator which delivers them to the drying floors above the continuous kiln, where about 100,000 bricks are being dried. The balance is dried in drying sheds around the kilns. The capacity of the plant is about 12,000 bricks per day.

In Figure 3, we have an outside view of the eighteen section ring kiln, improperly called tunnel-kiln in this country. Each section is about 10½ feet long by 6½ feet wide by 8 feet high, holding 4 000 bricks, equivalent to 6,400 American bricks. Three chambers are filled daily, and the kiln is turned in twelve to fourteen days. An Obel draft gauge is used for controlling the draft. The burning temperature is 1100°C. The kiln bottoms are solid, and side openings above the floor lead off the gases to the main draft flue in the center of the kiln. The fuel for the kiln as well as for power is brown coal briquettes about 2½ in. by 2 in. by 1½ in. and shaped as seen in Figure 4. Such fuel is used extensively in Germany. In this plant the briquettes cost $3.00 per

FIG. 6

ton, and the heating value is 5000 calories, or 9000 B. T. U. For power a "locomobile"—that is, a combined boiler and engine—of 54 H. P., is in use. In the development of locomobile engines, Germany is far ahead of America, and the water consumption per horse-power-hour has been reduced to approximately ten pounds compared with twenty-five to sixty pounds of water per horse-power-hour, which is the usual consumption in American clayworking plants.

There are about eighteen men employed in the factory from clay pit to finished product. The men in the pit are paid per load which figures about 50 pfennigs (12½ cents) per hour per man. The men in the factory received 22 pfennigs per hour and the burners and setters 30 pfennigs per hour. It costs about M 22.00 to make a thousand brick, and the average selling price is about M 30.00.

In concluding this plant, we wish to say a few words regarding the impurities of this clay and the treatment applied to overcome these and other difficulties. As mentioned, the clay is limey and in consequence of this, together with sulphurous anhydride in the combustion gases which are carried forward through the ware and moisture in the water-smoking compartments, sulphate of lime is formed. In the form of sulphate, the lime is rendered harmless so far as "popping" is concerned, but the ware is badly scummed by the lime sulphate. It is likely that some of the scum appears during the drying stage, but it is a well known fact that continuous kilns without advance heating flues increase scumming.

To reduce the scum, the firing of the kiln during the finishing stage is so conducted that the superficial lime sulphate is reduced, driving off the sulphurous anhydride, thus giving the caustic lime opportunity to combine with silica and alumina.

When the time for de-sulphurizing arrives it is necessary to have the fires clear, bright and uniform, then all dampers except one nearest the stack are tightly closed. The latter is used for regulating the reducing conditions. Now in each firing hole, as much fuel is dropped as experience has taught to be sufficient for finishing the ware (rather a little more than less) without melt-

FIG. 7

ing it. This firing has to be done quickly and is carried out when the burners change turns, so that two burners are available. After the feeding of fuel, some feeding holes ahead of the fire (two to five according to need) are uncovered in order to be able to judge from the rising smokey gases the condition of the operation. If very dark smoke appears ,one or two more feeding holes are uncovered to avoid the blackening of the brick. The first-mentioned open damper completes the regulation. It has to be regulated so that the smoke coming from the feed holes has a brownish-gray color. The gradual lowering of the damper is stopped when black smoke comes from the open feed holes. If, finally, in spite of lowering the damper, no black smoke issues, the damper is quickly lowered, and the feed holes closed.

In this condition, the kiln is left to itself for ten to twenty minutes. If now a feed hole cover is taken off, sulphur gas is coming out and the flame shows blue. If the color is very blue, the fire can be left to itself for one or two hours. If, after several trial openings of feed holes the flame gradually is taking on a reddish color, which means no sulphur present, then the dampers are gradually opened, and an oxidizing condition resumed to bring the bricks back to a finishing heat.

It is reasonable to suppose that this reducing action, if continued long enough, would penetrate the mass of the ware and reconvert the lime sulphate within the mass to caustic lime and cause popping. However, either the fine grinding has sufficiently overcome this danger or the reaction at the finishing temperature converts any caustic lime formed into a silicate body. What is accomplished is the reduction of the lime sulphate on the surface and its combination into a lime-iron silicate resulting in the characteristic buff lime-iron-silicate color.

There is an interesting brick and roofing tile plant combined with brown coal mine at Neustaedtel, Silesia.

The coal and the clay are both taken out of an open cut which on its bottom, about 130 feet below the surface, has several galleries driven into the coal bed. The clay and coal pockets are irregularly distributed and systematic operation is almost impossible.

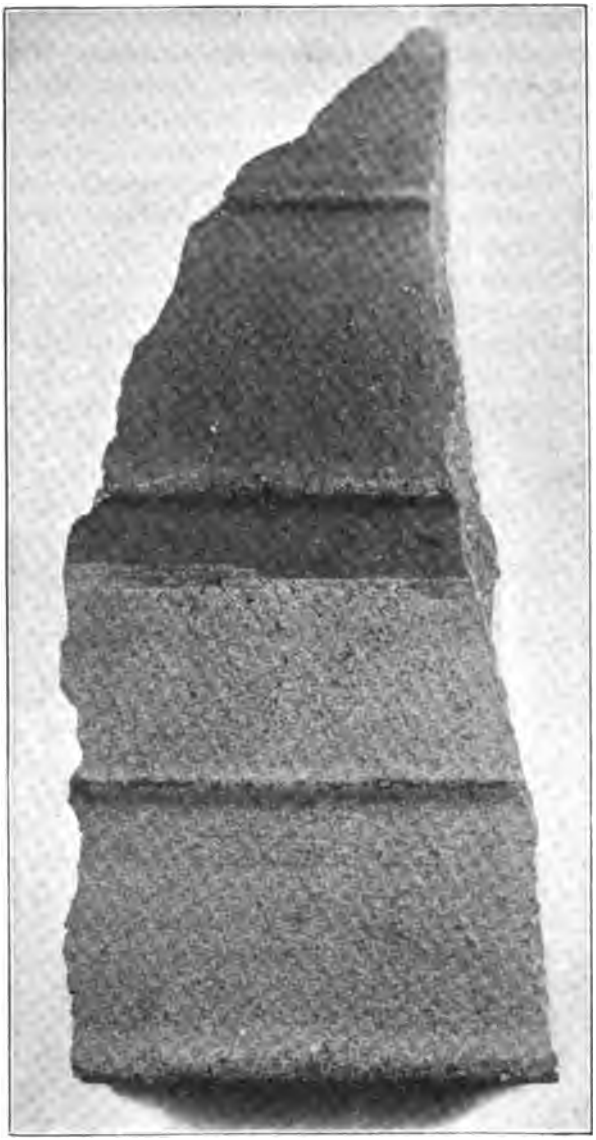


FIG. 8

The materials are taken out of the pit by a cable crane, illustrated in Figure 5. The cable is stretched over two inclined towers being a remarkable distance apart. The towers are provided with wheels and may be moved sideways upon a track. The cable has to carry the weight of the carriage and is counterbalanced by heavy concrete counter weights. The carriage has its motor for lifting the load, also for movement back and forth on the cable, and is provided with a cab for the operator, as can be seen in Figure 6.

At the bottom of the pit, the clay or coal is loaded into a box which then is hooked to the chains hanging from the carriage above. The operator then throws the switch, and the motor pulls up the load. After the load is up, the carriage is run by the same motor towards one tower where the box is emptied above a bin from where it is drawn into cars as is shown in Figure 7. While this is being done and the carriage is returning, a second box has been filled in the pit, thus avoiding any delays in the operation.

The coal cars are run to the separating plant, where an elevator picks up the coal from a pit. The separated coal falls into bins and from them is drawn off either into wagons or railroad cars.

The clay is moved to the factory and dumped into a disc feeder above a wet pan, below which is a set of smooth rolls, and then the auger machine. Elevating the clay in the first instance and then allowing it to flow by gravity to the brick machine is a common feature of German brick plants.

If roofing tiles are made, the column of clay from the first auger machine is broken off by hand and thrown into a second auger machine with a tile die. In front of the die, the bar is being coated with a thin layer of glue to prevent scumming. The white gypsum salts, drawn to the surface, are taken up by the glue and burn off with the glue. This preventative is also commended by Mr. Lovejoy in his treatise, "Scumming and Efflorescence."

I obtained a piece of tile on the plant which shows part without and part with the application of glue and the disappearance of scum is certainly noticeable, as Figure 8 shows.

After cutting, the tiles are placed on little pallets which are slipped into a frame, to be taken away by a lifting car, and wheeled into a tunnel dryer of the Keller type. The pallets rest on projections provided in the tunnel walls. For tiles all projections (about 3 inches apart) are used, while for bricks every other set of projections will receive a pallet.

Each tunnel is provided with three ribbed steam pipes, one being in the center of the track and one on either side, but all below the car on the ground. They are supplied with exhaust steam during the day and live steam during the night. There are 24 tunnels, and the clay being tender drying, it takes six days for the ware to dry. At the other end of the tunnels, the pallets are taken out in the same manner by lifting cars. After the tiles are removed from the pallets, the latter are then placed on a frame by women and taken back to the machine again. The brick and tiles are burned in a continuous kiln to cone 3-1100°C. The capacity of the plant is four million bricks per year and two and one-half million roofing tile.

NOTES ON THE BURNING OF SALT GLAZED SEWER PIPE

BY GEORGE D. MORRIS

The observations and experiments, enabling the writer to present these notes on burning and salt glazing of sewer pipe, were made on pipe manufactured from shale clay, and the principles have also been applied to pipe manufactured from fire clay.

The process for shale clay and fire-clay pipe can be divided into five distinct parts: first, water smoking; second, heating up; third, oxidation; fourth, vitrification; and fifth, glazing. These steps overlap more or less when applied to both shale clay and fire clay, although each will be treated separately.

Water Smoking. Water smoking is one of the most troublesome periods and is of much importance to the manufacturer of the larger sizes and double strength sewer pipe. The period covers the time from the start until the ware has given up all of the mechanically combined water and some of the chemically combined. In practice, this would invariably mean that the ware was bone dry or a little more. A temperature of about 350 degrees Fahrenheit would be obtained during this stage.

Successful water smoking of large size ware in a down-draft kiln should be done by using the kiln as a down-draft kiln, starting with very small fires and gradually increasing as fast as that particular clay will permit. Do not use the kiln as an up-draft, leaving the covers off for any length of time after starting the fires, unless the kiln is especially adapted, as when the kiln is covered a sudden change will result, and this, we are always striving to prevent during the burning of sewer pipe. The time of water-smoking varies from 24 to 96 hours, according to the size of the ware or difference in clay. A few of the effects of too rapid water smoking are as follows: scaling or blowing, blistering and cracked sockets. By scaling or blowing we refer to cases of large slabs blown off and found lying on floor of kiln. Too

rapid firing causes the outside to dry faster than the inside, and the unequal shrinkage causes the part drying fastest to break loose. Blistering is very common in clays that laminate. When the mechanically combined water is driven off, it collects under the layers of clay or blister formed during the pressing of ware, and if the water smoking is too rapid, the steam or gas will collect in these pockets, causing them to swell and sometimes to break open, forming scales on the pipe. In down-draft kilns, the pipe on the bottom are subjected to greater humidity or dampness, and we find on the bottom rows of pipe, the largest percentage of blisters. Cracked sockets is a common trouble when using excessive draft during water smoking. Currents of air are set up through the ware from excess draft, and the sockets dry faster than the body of pipe, causing a strain in the sockets which finally produce cracks. All of the troubles that arise in the water smoking generally occur in layers. The heat travels downward in layers, and we may have scaling or cracked sockets on the top pipe and none on the bottom, or vice-versa. Too rapid firing at the beginning will cause trouble with top pipe, too slow beginning followed by too rapid firing causes the trouble to occur on the bottom pipe. Many times it is necessary to increase the stack draft, by starting fires in the stack to warm them. Whenever the kiln bottom is very damp at the start of a burn, a built-in firebox in the stack is a very convenient arrangement for warming the flues, thus having a good draft at once.

Heating Up. Heating-up covers the time from water smoking to oxidation. In practice, it overlaps the other steps, as it is sometimes rather hard to designate without the assistance of a pyrometer. The heating-up period ranges from 350 to about 800 degrees Fahrenheit. In most plants, the drying is carried on gradually; and by giving plenty of time, oxidation starts at a low temperature, therefore not much time is left. If given special attention, a period can be produced where the temperature can be raised very rapidly from 350 to 800 degrees Fahrenheit without proving injurious to pipe. The following is a schedule for burning large size pipe at one of the large shale sewer-pipe plants:

Water smoking	0 degrees	to	350 degrees	in 72 hours.
Heating-up	350 degrees	to	800 degrees	in 24 hours.
Oxidation	800 degrees	to	1400 degrees	in 84 hours.
Vitrification 1400	degrees	to	2100 degrees	in 48 hours.

As this period is overlapped by the preceding and following periods, we will not dwell on it, as it is not altogether practical unless used by one of more than the average fireman's knowledge of burning.

Oxidation. Oxidation is a period of great importance to successful burning of shale clay, high in carbon but is usually not of great importance to the fire clay manufacturer except for the large sizes. Incomplete oxidation is very injurious to pipe, giving them a spongy interior, distorted shapes and inferior ring. The common supposition is, that incomplete oxidation is due to improper drying; and to remedy, a day or two days are added to the water smoking period. The result from such practice is that one kiln is well oxidized; and in the next one, the same old trouble will appear again. The best, easiest and surest way, is to adopt our goods friends', the brickmakers' "draw trial" system, and then with ordinary care, anyone can insure perfect burns as far as the complete oxidation is concerned. Draw trial should be made of the shoulder of pipe, which is the thickest part. The draw trials are placed near the door of kiln, so that on removing some of the brick from the door, the draw trials can be easily taken out. When the temperature nears 1000 degrees Fahrenheit (or just a little red at dusk), the progress of the burning out of the carbon can be noted. The trials are then drawn at regular intervals, until oxidation is complete. The temperature may be gradually increased up to about 1300 degrees Fahrenheit, and then held until trials are clear of carbon.

Vitrification. The vitrification period follows close upon oxidation, and if the oxidation is not completed before vitrification starts, there is little chance for its completion regardless of the amount of time taken for vitrification, for, when a thin layer of clay vitrifies on the surface of a body, no air can penetrate to the imprisoned carbon. As the temperature increases, the carbon

burns inside of the clay body, and as it must have oxygen to complete the combustion, carbon monoxide gas is generated, the oxygen being taken from surrounding particles containing oxygen. This gas being imprisoned in the intensely hot clay ware, which has almost reached a molten stage, will cause it to swell or bloat, and then we have the spongy interior and distorted shapes. The vitrification period covers two important steps as follows: making the required temperature within reasonable time, and a uniform distribution of heat over the entire kiln. The average time for vitrification is about 36 hours, starting at about 1400 degrees Fahrenheit and going up to about 2100 degrees Fahrenheit. This time will vary considerable, due to different kinds of coal, amount of draft, size and number of fire-boxes and to the nature of the clay. The writer has found that attempts to increase the temperature too rapidly at this period, require an excessive amount of cleaning of fires and this is likely to result in fire-cracking and crazing, especially during the early stages of vitrification. In the latter stages too rapid heat-increase will not permit uniform distribution throughout the ware in the kiln. In raising of the heat too fast, the necessary amount of air is not admitted for proper vitrification. Close firing results in reducing conditions, the heat remaining in the top part and burning the top pipe and outside ring of pipe too hard and causes the filling or stuffing, that is, small pipe inside of larger pipe are too soft. When glazing the ware in this condition, the top pipe may be very nice while the pipe one or two high from bottom and the stuffing are unglazed. By taking a reasonable amount of time in making the heat, allowing air to pass in over the fires and gradually reducing the draft, the heat will be conveyed from the fire-boxes and top of kiln to the middle, sides and bottom. By regulating the draft and leaving fires open, a soaking process is obtained, which is the holding of the temperature about uniform and distributing the heat uniformly throughout. The soaking process should begin as soon as the temperature and vitrification of the top pipes is sufficient for glazing; and then by the manipulation of drafts and fires, the temperature is held constant. No large amount of heat dare be

lost during the soaking period, for if the heat is lost, it is very difficult to regain it. When the soaking process is on, the draft is reduced to check the inrush of cold air, and by giving close attention to fires while the air is going in over them, the temperature can be held constant, and the heat conveyed from the fires to the bottom ware. By repeating the firing and checking of the draft, the heat can be brought to the bottom or floor of any kiln.

There are three common means of determining the temperature or degree of vitrification necessary for proper glazing: trials, cones, and pyrometer. The trials made from the clay can be used alone. The cones may be used alone, although they are sometimes greatly affected by the gases in the kiln, causing variation in their melting points. The pyrometer is very convenient and of great help in raising the temperature, but when the finishing time nears, and the time elements must be considered, the pyrometer only can give us the maximum temperature. The trials, cones and pyrometer used together serve as a check on each other; and too much care can not be taken, for the temperature or degree of vitrification must be right to obtain proper results. The cones and trials should be placed in the same place every time, near the door, so that trials can be easily removed. It is good practice to use two sets of trials and cones, one set about two feet from floor and the other about four feet from floor and both about five feet from door. With two sets, the distribution of heat can be checked with a greater degree of accuracy. The common practice is to raise the heat to that stage at which, when the trials are drawn and broken while hot, they show a glassy fracture. The clay is then very near the danger line and in a majority of cases has reached proper vitrification for glazing. The writer does not want to mislead anyone by this statement. However, in the clays which he has handled, this is a very good degree of vitrification for glazing, and with slight variation ought to prove correct for most clays from which sewer pipe are manufactured.

Glazing. The glazing of sewer pipe is not a difficult proposition, if the ware and kiln are in proper shape for glazing. It is only necessary to observe the different colors and sometimes the

roughness of ware that are found at one plant, to realize the different conditions of the kiln, gases and ware that must exist to produce these varied results. Starting with the ware at the proper degree of vitrification, clean fires and good draft, the salt is thrown upon the hottest part of fire, so that it will volatilize rapidly. The controlling of fire and draft are the vital points in securing a good glaze and smooth ware. Great care must be taken to produce "just right" conditions, as the "extremes" are dangerous. With too much draft, giving oxidizing conditions, the glaze will be very light, and it is generally difficult to maintain sufficient heat to burn the salt properly. On the other hand, not enough draft produces reduction, and if the clay contains particles of iron, with reduction these will fuse causing very rough ware. The medium of the two is what produces the fine glazed ware, and the other two, the off colors, light glazes, etc. The amount of salt and number of rounds will vary, although it seems that five or six applications ought to be enough for any clay. If it is not I would say, that the proper degree of vitrification was not obtained, though, of course, there are many reasons to cause the amount to vary considerably. The volatilizing of the salt requires a large amount of heat, and it is very seldom that the temperature increases during the salting, so that the proper vitrification ought to be obtained before starting the glazing. If the temperature shows any marked increase, the firing can be let up a little to check increase of temperature. The writer has seen kilns which have been salted from four to twenty times; and in all cases, where the heat was good and proper degree of vitrification had been obtained, the kilns salted four times were as good as the ones receiving the salt twenty times.

The cooling of sewer pipes will not be touched, as the writer heartily supports the methods of cooling given in Volume XVI of the *Transactions of the American Ceramic Society.*

The construction or arrangement of the kiln bottom exerts a very marked influence upon the burning and glazing of sewer pipe. There are so many different kiln bottoms, that they will not be discussed in this paper.

THE DEFORMATION OF PLASTIC BODIES UNDER COMPRESSION AS A MEASURE OF PLASTICITY[1]

BY WARREN E. EMLEY

From the standpoint of the user it frequently happens that the plasticity of lime, plaster of Paris, cement, or some kinds of clay, is the most important property of the material. A method of measuring plasticity is therefore, a necessity to the trade. Unfortunately, the term plasticity has been used rather loosely, so that while every one knows what it means, an exact definition would be rather difficult. It is hardly surprising, therefore, that there have been almost as many methods devised for measuring plasticity as there have been investigators.

The work of Bleininger and Ross on the "Flow of Clays Under Pressure," published in these Transactions last year, indicated that there is some definite relation between the plasticity of a clay and its behavior under pressure. It was thought that if a mathematical expression for this relation could be obtained, the results could be put on an absolute, rather than a comparative, basis and the method could be applied to materials other than clay.

To obtain this mathematical expression, recourse was had to Merriman's *Mechanics of Materials*, on page 378 of which is given a lucid explanation of the behavior of a plastic body under load, which may be stated briefly as follows:

If a material is subjected to compression, it will eventually rupture along certain well defined planes. If the material is non-fibrous and not extremely brittle, these planes will make some angle, θ with the vertical. Assume that the area under compression is unity, then the area of the plane of rupture will be $\frac{1}{\sin \theta}$. A load S applied vertically will be divided into two components: $S \cos \theta$, acting parallel to the plane and $S \sin \theta$ act-

[1] By permission of the Director, United States Bureau of Standards.

:he area of the plane, the intensi-
.rea are found to be, $S \cos\theta \sin\theta$
addition to the latter, there is a
s normal to the plane and holds
lly occurs by the slipping of sur-
.s plane; and, from the laws of

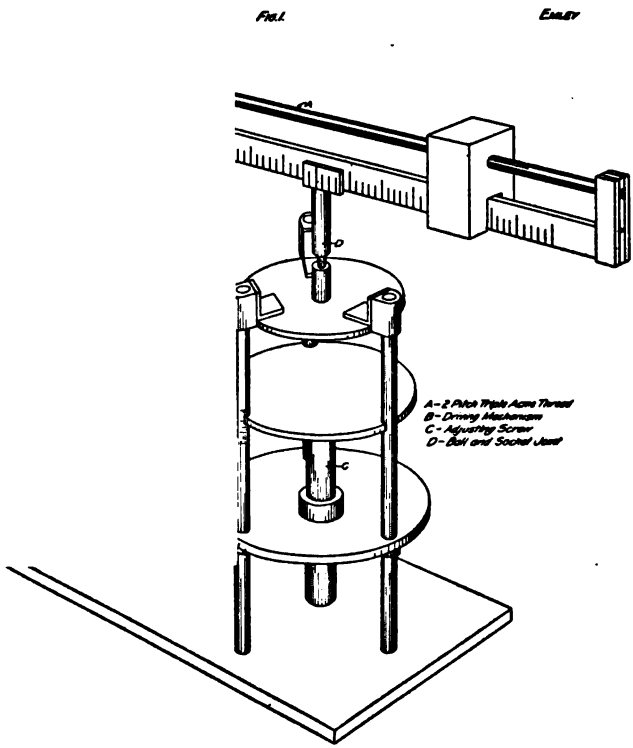


FIG. 1—ILLUSTRATION OF METHOD EMPLOYED

friction, we may, therefore, state that the force parallel to the plane is equal to the force normal to the plane, multiplied by the coefficient of friction. That is,

$$S \cos\theta \sin\theta = \eta\,(S_o + S \sin^2\theta).$$

Rupture will occur by motion along the lines of least resistance. That is, the plane of rupture will take up such a position that S

will be as small as possible. From the above equation,

$$S = \frac{\eta S_o}{\sin\theta\cos\theta - \eta\sin^2\theta}$$

and this expression will be a minimum when $\cot 2\theta = \eta$. Also, from the first equation,

$$S_o = \frac{S\tan\theta}{2\eta}$$

We have here mathematical expressions for the two important properties of the plastic body; η is the coefficient of internal friction; and S_o represents the force of cohesion between the particles. If η is high, the material will be sticky. If η is low, the material will be sandy. If S_o is low, the material will be difficult to work because it can be torn too easily. For the conditions of maximum plasticity, S_o should be as high as possible, and η neither too high nor too low.

The method of experimental procedure is extremely simple in principle, although all of the details have not been worked out yet. It consists merely of molding the plastic material, removing it immediately from the mold, and subjecting it to compression until rupture occurs. The necessary data include the angle which the plane of rupture makes with the vertical, the total load applied and the area under compression at the moment of rupture.

A number of experiments have been carried out in a crude way on samples of hydrated lime. These were molded in cylindrical form and placed on the pan of a Troemner solution balance. The top head could be adjusted and fastened in place by means of a set screw. The load was applied upwards by placing weights on the balance beam, and any deformation previous to rupture was taken up by lowering the top head. The load required to cause rupture was read directly; the area at the time of rupture was found by simple proportion from the final height, the original height and the original area; and the angle of the plane of rupture was measured by means of a comparometer.

So far as one can judge from working with the limes in the laboratory, and from their known reputations, the results ob-

tained from thirty-one samples of hydrate agree very well with practice. Thus, a sticky high calcium hydrate showed a value of $\eta = 0.8$, $S_o = 17.5$; for a dolomitic hydrate noted for its excellent plasticity, $\eta = 0.56$, $S_o = 32.5$; for a hydrate known to be short working and sandy, $\eta = 0.44$, $S_o = 17$.

On attempting to use this method for material other than hydrated lime, a number of difficulties were encountered. However, these are believed to be due to the empirical constants of the method, which can be readily changed. Thus, the specimens used were 1⅞ inches in diameter by 3 inches high, and the load was applied at the rate of 100 grams every 30 seconds. These conditions were found to be satisfactory for hydrated lime. With quick-lime or with clay, the deformation preceding rupture was so pronounced that the operator was kept busy lowering the top head so that the load could not be increased regularly. The rate of loading used is so slow that it is apparently impossible to obtain a definite point of rupture with some extremely plastic clays. It is believed that such difficulties can be overcome by changing the shape or size of the specimen and the rate of loading—a procedure which is permissible, if these factors are maintained constant throughout the whole series of experiments. For cement and plaster of Paris, the time of set must be taken into consideration, and some modification of the above method must be devised.

The crude method used has two serious mechanical difficulties: (1) The load should have been increased continuously, rather than by adding 100 grams every 30 seconds. (2) It was almost impossible to apply the load exactly parallel to the axis of the cylinder, so that the planes of rupture were usually found to make somewhat different angles on the opposite sides of the specimen. A machine is now being built which, it is hoped, will eliminate these troubles.

THE PHYSICS OF THE CLAY MOLECULE

BY R. F. MACMICHAEL

As a result of a series of experiments extending over a period of several years the following theories in regard to the plasticity of clay are advanced:

1. The plasticity of clay is due to the molecular cohesion of the clay particles themselves.

2. Fluids, other than water, develop plasticity in clay.

3. Organic matter, soluble salts, and colloids, except as the latter are considered to be merely very fine clay particles, are not essential to plasticity.

The observations upon which these statements are based are as follows:

Molecular cohesion is the immediate cause of strength of all materials. There is no other known force which can give strength to bodies. This force is radial in action, and its intensity varies inversely as the square of the distance separating the bodies. It has no known limits of action, the molecules of the sun attracting the molecules of the earth through a distance of millions of miles.

Molecular cohesion is the cause of the strength of dry clay, either directly, by the cohesion of the clay particles themselves, or indirectly through the medium of some foreign substance, which in turn derives its own strength from molecular cohesion.

Throughout this paper, it is assumed that the interposition of any foreign substance is unnecessary, and that clay derives its strength directly from the molecular cohesion of its own particles.

When water is added to dry clay, a disruptive force is developed, opposing cohesion and reducing the strength of the clay. If enough water is added to the clay, disintegration of the mass occurs, and slip is formed. In actual tests, the bars of wet clay are dried slowly, and the loss in weight and the gain in strength are noted from time to time.

The disruptive force of water is caused by the impact of the molecules of water on the clay grains, due to the heat vibration of the water. It is nearly proportional to the amount of water present and to the absolute temperature of the water.

Plasticity results from a balancing of the forces of disruption and cohesion, producing a peculiar combination of fluidity and rigidity in wet clay. Under light pressures, the mass acts as a rigid body. Under heavier pressures, it acts as an imperfect fluid. The slight rigidity of a mass of wet clay is due to the friction between the clay grains. Work is required to overcome this friction, so that a mass of clay when molded into shape retains its form, until acted on by a force sufficient to produce distortion. The fluidity of wet clay is due to the freedom of the individual particles of the clay to move over each other, after cohesion has been partially neutralized by the addition of water.

Actual contact between the clay grains, producing internal friction, is not incompatible with shrinkage. The latter implies only a re-arrangement of the clay grains in more compact form, in spaces previously occupied by water, in the same manner as three spheres may be so arranged that the over-all length can expand or contract without breaking contact.

As clay dries, the mass contracts under the force of molecular attraction, increasing in strength and rigidity and decreasing in volume. At the point where internal friction prevents further re-arrangement of the grains, shrinkage ceases. The increase in strength of clay in drying is due to the decreasing amount of water present and consequent lessening of the disruptive force, and to the smaller average distance separating the clay grains, thereby increasing cohesion.

As the temperature of clay is raised in burning, a new disruptive force appears. This is due to the molecular vibrations within the body of the clay grains themselves. It is similar to, but entirely separate and distinct from, the disruptive force of water.

Clay being a hydrated material has a compound molecule, containing in addition to the mineral matter present, one or more

molecules of water. As the temperature is raised, a point is reached where the attraction between the mineral components and the water molecule is no longer sufficient to hold the latter against the constantly increasing force of heat vibration, and the water molecule is thrown off in the form of steam. This is called dehydration. Though the vibrations of the water molecule are sufficient to cause dissociation from the general mass, and dispersion in gaseous form, the vibrations in the remaining mass are, as yet, so comparatively moderate that it still retains its solid form.

At this point, the cohesion of the mass when cooled is greater than the disruptive force of water. The mass does not disintegrate, and plasticity is destroyed. The organic matter of clay is also burned out at about this point. As in different clays, the organic matter may be burned out either before or after plasticity is destroyed, it does not appear that organic matter can be the cause of plasticity.

As the temperature is still further increased, the disruptive force of the heat vibrations overcomes the cohesion of the molecules of the dehydrated clay, causing the mass to soften, and producing a second state of plasticity. If substances are present which develop excessive vibratory action at comparatively low temperatures, or which form compounds which have this action, the cohesion of the mass is reduced and softening will take place earlier than would otherwise be the case. Such substances are known as fluxes.

The intense vibratory action at high temperature permits the re-arrangement of the constituents of the clay with the formation of new chemical compounds, and results in a great increase in the density and strength of the mass when cooled. This is known as vitrification. This closer contact also results in a diminution in volume, known as burning shrinkage. These changes are analagous to those observed in the drying of clay, and are produced by the same cause, i. e., atomic and molecular attraction.

If the above process is carried far enough, the clay will melt down to a thin liquid, permitting further re-arrangements of

the atoms and molecules to take place, with the formation of glass or glass-like products. In general, such compounds when cooled show very great strength and stability, with great resistance to disintegration from any cause.

The plasticity of unburned clay cannot be altered without altering the molecular structure. Water, acids, alkalis and organic solvents do not destroy the plastic properties of clay. This would probably not be the case, were the plasticity of clay due to the presence of some particular chemical substance other than the clay itself.

The adsorption or absorption of salts, oily impurities, and other similar materials by clay seems to be a case of solid or liquid solution or direct molecular adhesion. This general class of phenomena, under the names of occlusion, absorption, solution, alloying, amalgamation, and adhesion, is well known to chemists and physicists, and occurs in a very large number of substances.

Colloids and soluble salts, when added to dry powders in amounts sufficient to produce any notable effects, come to the surface on drying and form a hard shell. This shell is easily recognized and may cause serious cracking. There is no evidence of the formation of such a shell in the drying of ordinary clays. Neither does it appear, that the colloids heretofore extracted from clay by various means have been present in quantities sufficient to produce the necessary quantitative effects. As the quantity of soluble salts decreases during the formation of clay, while the plasticity increases, soluble salts would not seem to be the cause of the plasticity of clay.

If the plasticity and dry-strength of clays were due to the presence of colloids or organic matter, presumably some clays might be found in which these compounds had burned out before a sufficient quantity of mineral matter had fluxed to give the body an equivalent strength. Thus we would have clays stronger when dry than when partially burned. Or on the other hand, should the fluxing action of the minerals commence before such material had burned out, there would be a sudden rise in strength, followed by a less rapid rise or a fall. An examination

of a large number of clays has not shown a case of this kind. The curves of strength are smooth.

The strength of colloids, as of all other materials, is due to molecular attraction or cohesion. The adhesion of colloids to other materials as of glue to wood, or of paint to iron, is likewise a case of molecular attraction. This being so, presumably some material, such as clay in a finely divided state, may be found in which its own molecular cohesion may be sufficient in itself to produce the effects noted.

Silicic acid, sodium silicate, Portland cement, plaster of Paris and similar materials do not dissolve or disintegrate in water after setting, presumably because the force of molecular cohesion in these substances is greater than the disruptive force of water. In seeking a cause of plasticity, the colloids mentioned, silicic acid and sodium silicate, are not available owing to their irreversible set. They do not dissolve in water after setting.

Certain substances are plastic with either water or oil, and are about equally plastic with either. Oxide of iron, white lead, oxide of zinc, and whiting are such substances and are plastic in the order named. These substances are non-hydrated compounds. While oxide of iron, for example, is not as plastice as a good stoneware clay, it is more plastic than many clays used for common brick.

It would not seem that either colloids or soluble salts play any very important part in such cases.

Liquids, true solutions, and colloidal solutions, such as water, oil, glycerine, sugar syrup, and glue have very high temperature-viscosity coefficients. They are thin at high temperatures, and thicken very rapidly as the temperature falls, becoming solid or semi-solid at low temperatures. The change in viscosity in the substances mentioned is very great between the boiling point and the freezing point of water.

In clay slips, or soft mud, over the same range, the change in viscosity is hardly perceptible. That is, the thickness of the clay slip or the stiffness of soft mud is practically the same near the freezing point as near the boiling point. The slight change which is noted is just about what would be expected, owing to

the greater impact of the water molecules on the clay grains at higher temperatures. From this it would appear that the cohesion of clay is not due to the cohesion of a viscous liquid, but rather is due to the cohesion of the solid clay particles themselves, which would be only slightly decreased by the change in temperature through the range noted.

In the formation of clay from feldspar, disintegration, hydration, and leaching of soluble salts occurs. These processes are both physical and chemical in their nature, and result in the formation of a very large number of exceedingly small particles, the smallest of which presumably approach the dimensions of single molecules. Such particles are much finer than would ordinarily be produced by any strictly mechanical process. The properties of such particles would approximate the properties of the molecules composing them, and would show, to some extent at least, such phenomena as molecular attraction and cohesion. These properties would be transmitted in part to the entire mass of clay, as it is obviously not necessary for every particle to be of the smallest size, provided they are graduated from the largest to the smallest and the voids kept low.

Those clays containing the greatest number of fine particles would show the above properties to the greatest extent, which corresponds with ordinary observation, that fine grained clays are the most plastic. The toughness of wet ball clay is due to the ability of the fine rounded grains to slide over each other freely without breaking contact.

The shrinkage and the dry-strength of china clay are usually lower than would be expected from the plasticity test. This seems to be due to the fact that the grains are sharp and angular, and have not been rounded by abrasion, as in the case of transported clays. This sharpness of outline, while not affecting the plasticity test, which is made in the slip state, prevents the clay packing into a close, dense mass on drying, thereby reducing the shrinkage and the dry strength.

Shale is clay in which the grains have been forced into very close contact under pressure, so that water disintegrates the mass very slowly. Flint clay is similar to shale in that water does

not develop plasticity readily, if at all. Hot water (which has a greater disruptive force than cold water) and mechanical abrasion in the form of pugging, will develop plasticity more readily in these materials. Slate is clay in which partial vitrification has taken place under heat and pressure, so that water alone does not disintegrate the mass. It is, therefore, non-plastic.

The effect of pugging of soft clays is to drive the particles into close contact and to distribute the water uniformly throughout the mass. When these ends have been accomplished, further pugging within practical limits is useless. The pugging of hard clays such as ball clay or shales is continued until a sufficient quantity of fine material has been detached to give the mass the desired degree of plasticity. When such clays have been separated approximately into its individual grains, the maximum plasticity of the sample has been reached, and further pugging within any practical limits is without beneficial results. The individual clay grain is not softened upon the addition of water. Repeated wetting and pugging does not materially alter the size of the grains or change their general outline or appearance. This would not be the case, were the clay softened and reduced to a homogeneous mass upon wetting, and subsequently broken up with the formation of new grains when dried and ground.

Whether wet or dry, under the microscope, the grain retains its appearance of a hard, sharply outlined body.

The weathering of clay on the dump is a continuation of the natural processes of disintegration, leaching and hydration, and with certain types of clay may be very beneficial.

That plasticity is not dependent on the mechanically mixed water, is shown by the fact that other fluids develop this property. Among these are anhydrous sulphuric acid, anhydrous nitric acid, absolute alcohol, and glycerine. Each of these fluids is soluble in water. There is no evidence of any essential chemical action having taken place, as the clay may be dried and made plastic again with any of the other fluids.

Ether, gasoline, kerosene, engine oil and similar liquids, form an inhibitory coating over the clay grain, and prevent the display of plastic properties. These liquids are insoluble in

water. Though these liquids are to some extent able to prevent the formation of the plastic bond, they are unable to break this bond once it has been formed.

It seems probable that in the drying of clay, cohesion reaches a high value owing to the fact that the ultimate film of water adhering to the clay grain is removed, through the body of the grain itself, to the surface where it evaporates. This occurs either directly through intermolecular spaces, or indirectly through the interchange of atoms or ions, with the chemically combined water of the clay. The surfaces of many of the clay grains are probably very rough as compared with the size of the water molecules. These molecules cannot be squeezed out by pressure alone, and unless properly disposed of, remain to exert their disruptive force and prevent cohesion reaching any very high value. This same action is seen in the drying of the hands, which cannot be dried by pressure alone, but must be brought into contact with some absorbent material. In a similar manner gold leaf, which has a higher cohesion value than clay, cannot be welded satisfactorily until after the moisture has been removed.

Silica and feldspar, not being hydrated compounds, do not permit the passage of water and therefore do not cohere readily. Also it seems probable that the rough crystalline faces of these materials prevent any very close contact, as is the case with china clay. Oils, and liquids insoluble in water do not dissolve or dissociate, and therefore remain on the faces of the clay grains preventing cohesion.

Under ordinary conditions, the clay grains in a slip settle slowly to the bottom. This period of settling may range from a few minutes for coarse clay and sand, to several days or even weeks and months for very fine particles. Particles below a certain size do not settle of themselves, but are held in permanent suspension by the molecular movements of the water. When an electrolyte, such as hydrochloric acid or nitric acid, is added to a slip, the attraction between the fine clay particles is increased, causing them to group together into more compact masses. This is known as flocculation.

When other electrolytes, such as sodium carbonate or ammonia, are added, the process is reversed. The individual particles separate and remain suspended upon agitation, causing the slip to thicken. This is known as deflocculation. These processes are electrostatic phenomena, and are observed in many substances when suspended in water in a finely divided state.

These forces, while producing large and striking effects in thin slips, are in reality quite small as compared with the forces acting in soft mud and in dry clay. In the former case, the principal effect seems to be that a greater or less quantity of water will produce an equal degree of fluidity. This effect is taken advantage of in trades using the casting process.

The thickness, or viscosity of a clay slip, when in a state of maximum deflocculation, is an indication of the plasticity of the clay.

Mechanical pressure alone, without the use of a liquid of any sort, will produce cohesion and dry-strength in clay. This is shown by the action of dry powdered clay in a briquetting or tablet forming machine, or by the compression of the clay under the blow of a hammer.

In such cases, the only possible explanation seems to be direct molecular cohesion, as the action of colloids, soluble salts, and organic matter in any way heretofore suggested, requires the use of a liquid. All matter in the solid or liquid state shows this same action to a greater or less degree, and may be made to cohere under suitable conditions.

The force producing cohesion seems to be identical with that of chemical affinity, which causes atoms to combine into molecules; with molecular attraction which causes molecules to combine into masses and gives strength to these masses; and with the force of gravity, which gives weight to bodies and which acts through interstellar spaces.

In conclusion, it does not seem necessary to assign to clay any peculiar properties not found in ordinary matter. Neither does it appear necessary to pursue a search for a mysterious and elusive substance to mix with the clay grains to make them stick together.

Molecular cohesion alone as outlined above is sufficient to produce the effects noted, and is held to be the prime cause of the plasticity of clay.

DISCUSSION

Prof. Parmelee: I would like to ask some of our potters their experience regarding the relative merits of pugging and storing the clay in the cellar. As I understand Mr. McMichael's paper, he says that the pugging will give the same advantages as the storing. Mr. Mellor, has that been your experience?

Mr. Mellor: No sir, that has not been my experience. The aging of clay before it is pugged has a very strong tendency to increase the plasticity and good working qualities of the body, as we understand it, and that's a decided advantage to both workman and manufacturer. On the other hand, we can take clay that is in good condition in our cellar or storing places, and very often pugging, if it is not correctly and finely adjusted, will destroy that very plasticity and give us a granular or non-plastic condition. That has been my experience.

Mr. Mayer: You can go on pugging clay until you can't work it at all; that is exactly my experience.

Mr. Purdy: Let me have that again.

Mr. Mayer: I say if you go on pugging clay long enough, you couldn't work it at all.

Mr. Watts: I would like to say also that the statement regarding the size of the grain is hardly justified, because I can produce clays which are shown to be uniformly of very much smaller grain than any of the normal ball clays or china clays, and yet they are absolutely devoid of anything we can really classify as plasticity. For instance, some of the clays of Georgia, some of those bauxitic clays, as soon as they begin to dry out a little, they have no strength at all, they just fall down like a lot of fine sand.

Mr. McMichael: In answer to Prof. Watts, it has been my experience that there are a great many fine clays which contain

fine sand. A definite distinction must be made between sand and clay. Such clays may be very largely non-plastic.

In regard to the question of aging, our experience has been this. Our tests have never shown any difference, and there is not a man on the plant today who can consistently tell pugged clay which has been aged, from pugged clay which has not been aged. I refer here to soft clays, not shales, or fine grained strong ball clays. The latter continue to develop greater apparent plasticity with either pugging or aging until separated into approximately their individual grains.

Obviously, as has been suggested, there may be a point which is the most suitable for working by any particular process, but the general action in either case is very much the same, that is, the softening of the aggregates and the separation to a greater or less degree into individual grains.

DISCUSSION CONTRIBUTED AFTER READING THE PAPER

Mr. Purdy: Mr. McMichael is correct when he says that plasticity is not due to colloids except as the latter are considered to be merely fine clay particles.

I believe he is in error when he says plasticity is due altogether to a balancing of the force of molecular cohesion of the clay particles and the disruptive force of the water of plasticity. I say that I believe he is in error in this theory, for I cannot understand the disruptive force of the water of plasticity.

The Misses "Sol" and "Gel" have flirted with us a long time, but they are as illusive as ever and are rapidly losing rather than gaining admirers. Those, who are still loyal to them, admit, that they belong to the "fine grain" species and owe their right to the nick-name of colloid wholly to similarity in reaction with electrolytes. There is no other parallelism in their make-up or properties. Of these two clay colloids, Miss Gel is the most ridiculous impostor that has attempted to gain

our serious considerations. A salt in solution is merely a salt in solution when mixed with water alone, but becomes a gel colloid when clay is added to the solution. This Miss "Gel" is credited with a reversible character, a sort of Dr. Jeykle and Mr. Hyde peculiarity. I do not deny the existence of gels, but I cannot see how clay can cause this reversibility in state from gel to ordinary solution.

Mr. Ashley, whose memory I hold very dear, published a formula (*Trans. Amer. Cer. Soc.*, Vol. XI, p. 530) and declared a doctrine founded on the one parallelism between clays and colloids, by which he could prove that some sands are as plastic as any known clay. There may be more ridiculous doctrines than this, but I don't know of them. If any exists, I sincerely hope that we innocent minded ceramists may be spared from further impositions.

Then sols are fine grains and the gels are adsorbed salts. These are old friends of ours whom they wish to masquerade under high brow nick-names.

I note that Mr. McMichael has marshalled heat vibrations of water as a factor in causing plasticity. His idea here, I take it, is that the heat vibrations cause greater mobility. Hot sand will flow much easier and have much less angle of repose than cold sand. If there is a connection in principle, between the fact of greater flowage of hot sands and Mr. McMichael's heat vibrations, I cannot see it.

If opportunity were given me to rewrite my theory of plasticity which I announced in discussion of Ashley's paper, Vol. XI, p. 555, I would leave out some of the non-essentials, but I would still hold fast to the "fineness of grain—adsorbed salt" argument. My arguments are the same as those who hold the colloid theory, except that they go further by saying that a material having these characteristics must be colloidal, and the fine grains should be honored by the title sol, and the adsorbed salts by the title gel. In doing this, the colloidal theorists go beyond the measureable and understandable to indulge in high brow speculation of which they know not.

Mr. MacMichael: Water does produce a disruptive force in clay. This is beyond dispute, as may be seen in Table I. The obvious cause to which to attribute this action is the kinetic energy of the water molecules.

The quantitative proof of the above is that hot water, in which the heat energy is greater, produces a greater effect than cold water. Thus hot water dissolves many hard fine-grained clays much more easily than cold water.

I cannot discuss sols and gels in relation to clay as I have never seen any evidence of their existence.

TABLE I—DRYING TEST ON ONE-HALF INCH BARS

PLASTICITY, 1.6. DRY LENGTH—94 PERCENT.

WATER IN TERMS OF DRY CLAY	STRENGTH PER SQUARE INCH	REMARKS
percent	*pounds*	
0	490	Dried at 212°F.
4.7	370	Air dried at 65°F.
7.	300	Feels dry.
8	250	Looks dry, but feels cold.
12	170	Turning gray. Past leather hard.
14	140	Sharp break; looks dry on ends. Shrinkage all out.
16	100	Leather hard.
18	50	Slightly brittle.
20	30	Rather stiff.
21	15	Flows easily.
22	1	Soft mud.
30	...	Very soft mud.
45	...	Thick slip.

EXPERIMENTS IN CASTING HEAVY PIECES OF PORCELAIN FOR ELECTRICAL PURPOSES

BY HUGO J. LUNDGREN

Last year the writer made a series of experiments in order to determine whether an improvement could be made in the method of casting such heavy pieces as are used in the electrical industry for insulation of high tension apparatus, for example those shown in Figures 1 and 2.

The process of casting ware of this kind has been used by several manufacturers for years and is considered to produce as good porcelain for electrical purposes if not better than that made by other methods of producing wet-process ware.

It seems, however, that this method has been limited to pieces of a uniform thickness of less than one inch, and to pieces that allow free shrinkage in the mold. The following experiments were made to discover a method which would overcome such limitations, but it should be noted that the facilities and apparatus of a laboratory were not available, and, therefore, some of the problems were not investigated as well as they might have been. No definite plan was followed, and whenever difficulties were encountered, many trials of widely differing nature, were made in the endeavor to overcome them. Only those experiments which seem of value in reaching the final result will be mentioned.

The following experiment was made to determine the exact amount of soda required to produce the most liquid slip: Five samples of 50 grams each of dried clay were put into five bottles and 50 cc. fluid were added to each sample. To No. 1, pure water was added; to No. 2, 47 cc. water and 3 cc. soda solution (5 grams soda per 1000 cc. water); to No. 3, 45 cc. water and 5 cc. of the soda solution; to No. 4, 40 cc. of water and 10 cc. of solution; and to No. 5, 35 cc. of water and 15 cc. of solution were added. Each bottle was properly labeled and shaken until the clay was well stirred up, then it was allowed to stand until the following

day After a thorough shaking next day, it was found that sample No. 4 with 40 cc. of water and 10 cc. of solution appeared to be most liquified, which fact was indicated by the greater noise when shaken and by the way the slip poured. Each sample was then rubbed or poured through an 80 mesh sieve and tested in a similar way, and this test again proved that sample No. 4 had a decided advantage over the others. Several bodies having different ratios of ball to china clay were tried in this way, and all showed about the same behavior. Therefore the standard body as used for other ware in the factory was selected for this investigation.

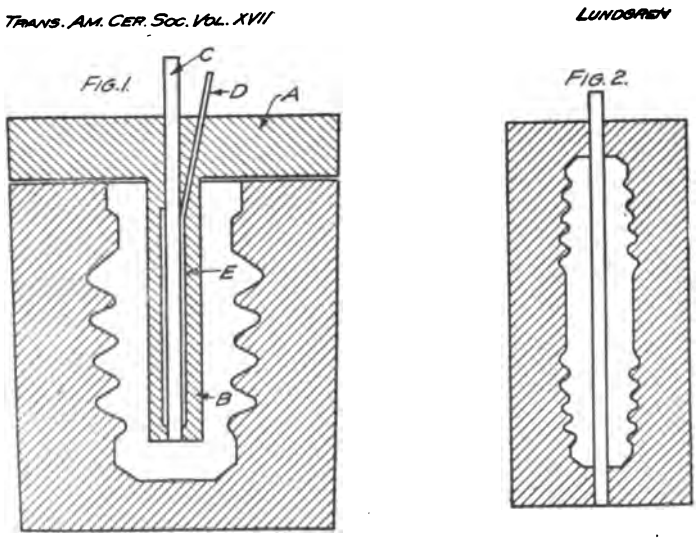
The casting was now started with a piece as shown in Fig. 1, but with a mold in only two parts as ordinarily used. It was soon clear that something had to be done to obtain the proper thickness within a reasonable time. At first, the mold was made so that the casting could be done by the pressure of a column of the slip, different pressures being obtained by varying the height of the column. This, however, did not fully accomplish the results anticipated, therefore casting with a core, as illustrated in Fig. 1, was then tried.

The plaster of Paris mold is made in three parts, the top part A, and the core B being made in one piece. The mold is clamped together and the slip is conveyed into it through the tube C by means of a rubber hose attached to the top of the tube. As the mold is filled, the air escapes at the top between the sections. The draining of the slip is now done through the absorption of water by the core as well as by the outer mold, and it is obvious that this should facilitate the casting considerably.

When opening the mold, it will be found that the clay sticks to the core so that a special method must be employed in order to take out the latter. This can be accomplished, if compressed air is led through the tube, D, into the hollow space, E, in the core. The air and the moisture of the core are forced through the porous plaster and press the clay from the core, so that, after the air pressure has been maintained for a couple of minutes, the core can easily be pulled out. The casting can then be taken out of the mold in the usual way. The air pressure remains on

the core for a short time after it has been removed from the casting. By this means the core is sufficiently dried that it may be used repeatedly without other means of drying.

A number of experiments with this new mold were made; and as only small quantities of clay were mixed up each time, several batches were used. By chance, a slip was obtained that showed a great difference from previous ones. It had a tenacious consistency like syrup, but would flow so easily that the mold had to fit very tightly to prevent it from leaking out, and it



would stiffen so quickly in the mold that the casting could be removed after about two hours. Speculations as to the cause of the different behavior of the same slip under apparently the same conditions led to the measuring of its specific gravity. It was found, that the specific gravity of two slips of the same body and apparently the same consistency would vary as much as .5, a slip having a specific gravity of 1.45 might not flow very well, while a slip of 1.90 specific gravity might flow excellently. It was also found that a slip of 1.90 specific gravity would not

stiffen so quickly as one of 1.80 specific gravity. In order to determine the best specific gravity, a few experiments with slips of different specific gravities were made. The result indicates that a specific gravity of 1.82 to 1.85 would be the most favorable. A large quantity of slip of this specific gravity was made up on a blunger, and about 250 pieces such as shown in Fig. 1 were cast without difficulty.

Larger pieces were also made. The largest one was a bushing similar to Fig. 2, having a maximum diameter of 5½ inches and about 22 inches long, with a cylindrical hole of 1 inch diameter. The hole was made by means of a brass tube. The bushing could be removed from the mold after five hours, although, as shown by the above dimensions, the maximum thickness of wall was 2¼ inches.

It is the writer's opinion, therefore, that the method of casting can be successfully employed in making large pieces for electrical purposes. Casting of pieces of several feet in length should be possible if the mold is divided into sections of about two feet in length, even though the shape does not permit of any shrinkage in the mold. A thickness of two inches can easily be obtained without a core, and with a core, it ought to be just as easy to get a thickness of three to four inches.

There is, however one difficulty that so far has not been entirely overcome, and it is in the hope that some light may be cast upon it that the writer has brought the matter before the Society. It has been found that small projections appear near the surface whether the ware is glazed or unglazed. If the piece is broken for examination through one of these places, it will be seen that the material has been ruptured, as if some gas had developed in the clay during the burning, after vitrification had started or taken place. The appearance indicates that it was not caused by air bubbles. A soft bisquiting seems to diminish the trouble, but it does not overcome it entirely. The percentage of faulty pieces also varies in different burns, averaging from five to twenty percent.

DISCUSSION

Prof. Parmelee: Mr. Lundgren has a piece of the ware showing a blister on the surface formed apparently after the ware had reached a state of vitrification.

Mr. McDougal: We had some trouble with the same thing, and I went down to Prof. Bleininger with it, and he advised several methods of overcoming it, one of which proved to be very successful. Those blisters are undoubtedly caused by the soluble salts in the body which are carried toward the mold, as the piece is cast and as it dries, especially as the piece dries on the stilliards. The salts are carried to the surface with the water which is evaporating from the pores. If the piece then, is not finished, and well finished, by sandpapering or very good sponging, this salt will remain deposited near the surface and will give this sort of glazed coating which, in a bad case, will give blistering when the piece is fired in the kiln. In my opinion, this blister was formed by the relatively more fusible coating on the outside of the ware, which coating was formed by the salts carried to the surface in the drying.

Mr. Lundgren: The blisters usually occur at a depth of between one-sixteenth and one-eighth of an inch under the surface. It does not seem likely to me that the salts in the clay would cause blisters at that depth.

Mr. McDougal: There is no doubt but what some salts are dropped all along the line and probably the percentage carried clear to the surface would vary with the rate of drying and probably with other variable conditions.

Mr. Lundgren: That might be possible, but it is not clear to me why the salt accumulates at certain points so as to cause blisters. It seems reasonable to believe that all salts present are dissolved and, therefore, must be uniformly distributed throughout the clay inside of the piece. On the surface of course the salts will crystallize out as the water evaporated.

Prof. Parmelee: In the sample I saw, Mr. McDougal, the cavity was very large as large as the end of a lead pencil, at least, and presuming that your view is correct, there must have

been a considerable accumulation of salts there, a much larger accumulation than I suspected, under such conditions.

Mr. McDougal: We got away from the same thing, that is, this intensive blistering, by sandpapering the piece after it had become absolutely dry, after which, there would be no chance for further salts to travel to the surface.

Mr. Lundgren: I would like to ask how much was taken off from the ware?

Mr. McDougal: Perhaps one thirty-second to one-sixteenth of an inch. A rather abundant source of blistering in casted wares is an enclosed hollow cast. This is caused by the source of the slip being shut off from a part of the piece, before this part has finished casting. The result is an air space which expands with the heat of the kiln and produces blisters in the ware.

Mr. Purdy: Taken off by the sandpapering?

Mr. Lundgren: Yes.

Prof. Parmelee: These were found at the depth of a sixteenth to an eighth of an inch?

Mr. Lundgren: Yes, as far as my observations go, not deeper than one-eighth of an inch. Perhaps the gas that is believed to be developed in the clay has not the power to cause a rupture at a greater depth.

I want to say also, in this connection, that about two hundred pieces had to be turned off about one-eighth of an inch at a certain place in order to fit some iron clamps. The blisters, however, occurred also where these pieces had been turned off, a fact that seems to speak strongly against the theory that the blisters were caused by the salts.

Mr. Purdy: I don't want to get away from the subject, but this blistering has been interesting to me. In floor tile manufacture, where they made floor tiles by the dry press process entirely, mixing the bodies in a ball mill and dampening them on plaster tablets, using china clay and feldspar or ball clay and feldspar, we had blisters that were not due to overfiring, nor to

the plaster dampening tables, for they would come from all parts of the kiln and when not dampened or on the plaster table. I have often wondered what caused blisters in porcelain.

Mr. Mayer: They treated this subject entirely from a casting standpoint. What about the manufacturer in the ordinary body? What about the question of blistering there? We were for three years entirely free from blisters, it was practically unknown. Then, we ran out of a certain kind of Tennessee ball clay and began using English ball clay, and just as soon as we did that, we got into it right up to the neck. As we have reduced the English ball clay, we have reduced our blistering and are trying to throw it out altogether. That was our experience. For three years, I would not use a particle of English ball clay in our vitrified body, and I don't know that I have a right to assume that it was English ball clay that caused the blistering, but it is a fact, that since we cut it out, we got less of it. There is no question of casting salts in that at all, only such soluble matter as you get in the ball clay.

Mr. Lundgren: That is very interesting, Mr. Mayer. I used English ball clay, but I never thought of looking for trouble there. Perhaps a change in ball clay will overcome the difficulty.

I have been concentrating my attention upon the burning process. As I said in my paper, the percentage of faulty pieces varies in different burns, and also different places in the kiln seems to affect the blistering differently. The ball clay I used had a lot of coal impurities and although the slip was put through a fine lawn, it is possible that some of these impurities passed through and became included in the casting slip. If then during the burning process a reducing atmosphere were maintained until vitrification had started these impurities could not burn out. But if then, just after the vitrification had started, the kiln atmosphere became oxidizing, is it not likely that some oxygen would penetrate the ware at least to some depth, burn the coal impurities and develop gases that would cause these ruptures?

I tried to regulate the burning in order to eliminate this possibility, but fear of endangering the quality of the other ware in the kiln through a great change and inadequate means of regu-

lating the firing may account for my failure to make any progress in this way.

Mr. Blair: I don't know, whether the blistering, under discussion, is similar to the blistering we have in stiff-mud ware or not, but our experience in stiff-mud ware might throw some light on it. My observation has been, that blistering in that class of ware is largely a mechanical defect, or a lack of bond between the outer skin and the inner body of the material in the green state; and that lack of bond is induced in stiff, hard ware simply by die friction, the blisters not showing up probably until the ware is partly dry. In other cases, we find the blisters showing on the green column, and that is one of the deadly defects that we find in the manufacture of common art tile and has to be watched very carefully. It can usually be traced to some mechanical lack of bond on the surface, or just under the skin of the ware, which is puffed out either by the evaporation of water in the drying process or the compression of the entrapped air which occurs while the clay is coming through the die, and later the expansion of that air under the thin film on the surface of the ware.

Now, it is just possible, that blistering on glazes might arise from a lack of bonds between the glaze and the body, which is not noticed in the green state, but leaves a weak spot which would later develop by the expulsion of gases or something of that kind.

On a thin piece of ware, such as the tile I have in my hand, the surface strain produced by the friction of the die, is very severe, and the skin surface is a good deal like a piece of rubber, it will stretch, and if the lubrication is perfect, and the bond is perfect, it stays down, but if you get a little volume of air in the body next to the surface, or a piece of clay which is of different density or anything of that kind, that rubber skin will stretch and puff up again when the pressure is released. The cure, that I have found for that defect, is to put weight enough on it to hold it down and keep the weight on it, until the bond is re-established in the kiln. That, in pottery ware, of course, is an

impossibility, because you haven't the surface that you can apply the weight to, but in flat ware, it is entirely possible.

Mr. Purdy: I would like to ask if Mr. Lundgren finds any difficulty in getting all the flanges or petticoats by this casting process?

Mr. Lundgren: There is no difficulty in that; the kern is first taken off, then the other parts opened and the casting can be removed easily.

Mr. Purdy: What I mean is, will the casting creep up along the surface of the mold all right?

Mr. Lundgren: Yes, certainly the slip will creep into every little crack in the mold.

Mr. Purdy: Must you take any special care in getting it to fill the mold?

Mr. Lundgren: No.

Mr. Purdy: I would like to ask how many castings you get out of a mold?

Mr. Lundgren: I don't know. I have taken hundreds of pieces, as indicated in Fig. 1, from my molds, and they are still in good condition.

Mr. Purdy: One mold per day?

Mr. Lundgren: You could make four or five from Fig. 1 mold, and one or two from Fig. 2 mold, per day.

Mr. Weelans: The blistering proposition in our business comes from various causes. I would like to ask Mr. Lundgren whether he changed his fluxes in the body at times, to discover whether or not that had anything to do with the blistering?

Mr. Lundgren: No, I have not done that.

Mr. Weelans: Do you know whether it was a case of overfiring?

Mr. Lundgren: That is possible but not very probable.

Mr. Weelans: Judging from the character of the piece, I think it would indicate that a little more refractory material, in there, would obviate the cause of blistering in this case, al-

though there are so many causes, that it is a pretty indefinite proposition, but that is what the trial indicates to me.

Mr. Lundgren: That's a new and interesting way of looking at it, but if I should increase the refractories in the body, would there not be the risk of getting the ware under vitrified in some places of the kiln, which would seriously affect the insulating quality?

THE TESTING OF CLAY

BY R. F. MAC MICHAEL

The object of clay testing is to determine the uses to which a clay may be put, the methods best adapted for handling the clay, and to maintain a check on the supplies of raw material and on factory processes.

The best results in clay testing will probably be obtained by systematic procedure in a laboratory especially equipped for the purpose, the results to be tabulated and to be expressed by figures and curves in permanent form on a regular printed blank.

The following methods have been found satisfactory: The general physical characteristics of the raw clay are first noted, and recorded as indicated on the accompanying test sheet. These include color, hardness, fracture, uniformity, organic matter, foreign material, behavior in crushing, pugging, and forcing through dies, and remarks of a general nature.

Plasticity is determined by noting the amount of water required to form a slip of standard thickness or viscosity. The clay is blunged, flocculated to its maximum viscosity with an electrolyte, and diluted with water to a standard thickness. The amount of water contained in the slip is determined. If a flocculating agent, such as hydrochloric acid, is not used, other adverse electrolytes, which are frequently present, prevent the slip attaining maximum value, and erratic results will be shown.

Attempts to determine the plasticity of clay on soft mud samples do not give satisfactory results, owing to the large and indeterminate influence of the non-plastic material present. The viscosimeter illustrated in Figure 2, was developed especially for this work. It is rapid, accurate and easily manipulated and is not influenced by variations in specific gravity, or by the presence of sand or foreign materials, even if present in quite large amounts.

The standard of viscosity for the clay slip is taken as ten times the viscosity of water at 20°C. or 68°F. Hydrochloric acid is used for flocculation.

The wet strength of the clay is determined in the multiple briquette machine, breaking five samples at once, as illustrated in Figure 3. A bar of clay is expelled through a figure eight die and cut transversely with a gang cutter into samples having a net area of one square inch. Sand flowing through automatic valves is used for breaking, the average of ten samples being taken.

One hundred grams of clay are blunged into a thin slip and sieved through a two hundred mesh screen. The plus two hundred mesh material is caught on the screen, removed and dried, and the weight and character noted.

The minus two hundred mesh material passes through the screen into a half-gallon crock below, and is dried at about 160°F., and the weight and character noted.

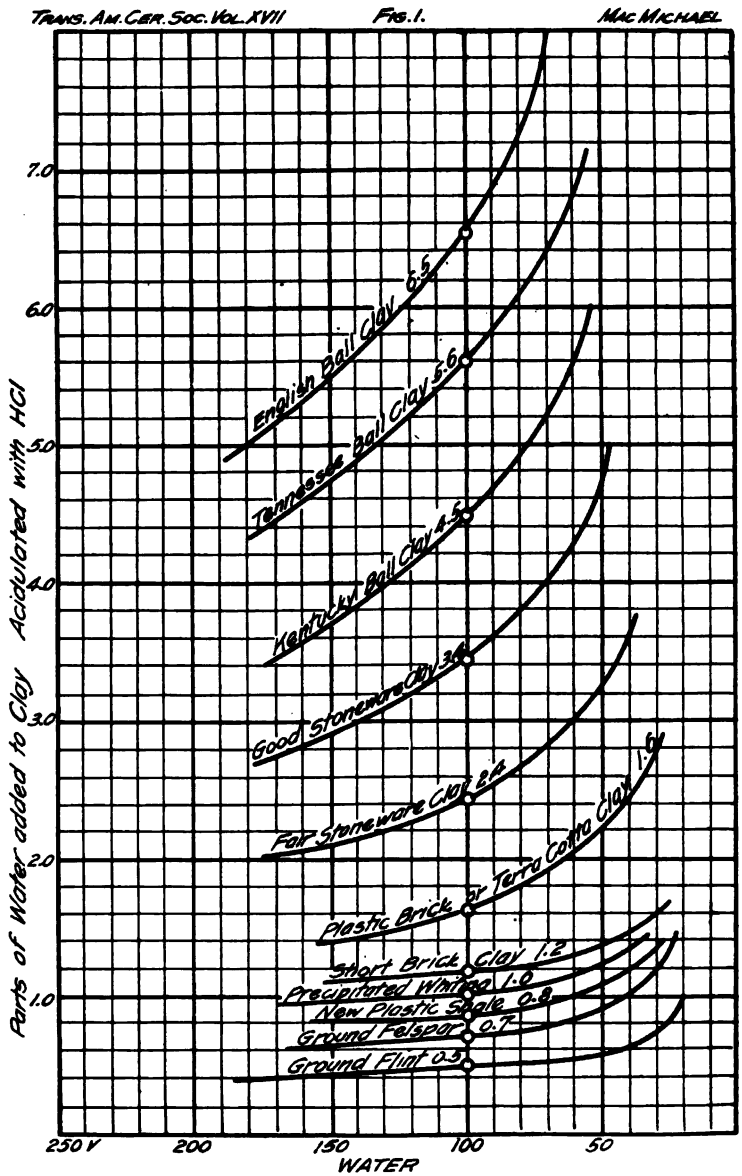
Chemical analysis is not ordinarily made, though a blank space is provided for this information.

One hundred grams of wet clay are pressed into a briquette and dried at 160°F., under standard conditions. A balance and shrinkage gauge, as shown in Figure 4. indicates the loss of weight and the shrinkage simultaneously. These values are noted from time to time on the test sheet and the drying curve is plotted as shown. If cracking develops during this test, it is noted on the forms. See Figures 5 and 6. A hundred gram sample is found satisfactory, and in connection with the other information noted gives an excellent idea of the drying properties of a clay.

Bars one-half inch in diameter are expressed on to a grooved board and cut into five inch lengths. The bars are stamped with a sample number and notched with a hundred millimeter gauge as shown in Figure 7, and the average wet weight is noted.

The samples on the rack are placed in a drier at 160°F., and dried under standard conditions. Should warping of the ware be likely to occur under ordinary commercial conditions, it will very probably be shown in this test.

Several of the dry sample bars are broken in the testing machine illustrated in Figure 8. The broken sample, near the


TRANS. AM. CER. SOC. VOL. XVII
FIG. 1.
MAC MICHAEL
Parts of Water added to Cloy Acidulated with HCl
7.0
6.0
5.0
4.0
3.0
2.0
1.0
250 V
200
150
100
50
WATER
English Ball Clay 6.5
Tennessee Ball Clay 5.6
Kentucky Ball Clay 4.5
Good Stoneware Clay 3.6
Fair Stoneware Clay 2.6
Plastic Brick or Terra Cotta Clay 1.6
Short Brick Clay 1.2
Precipitated Whiting 1.0
New Plastic Shale 0.8
Ground Felspar 0.7
Ground Flint 0.3

point of fracture is dropped into the "V" gauge shown in Figure 9, and the factor opposite the center of the bar noted. This factor multiplied by the breaking weight gives the strength of the bar, in transverse rupture in pounds to square inch. This strength corresponds very closely to the actual tensile strength of the clay, and successive tests will be found to check satisfactorily.

The burned-strength is later determined in a similar manner.

The dry-shrinkage of the clay is measured with a millimeter scale, each millimeter representing one percent shrinkage. The dry shrinkage of the bars is slightly greater than that of the sample, but as it seems to correspond more closely with the results obtained in actual commercial work, it is this value which is referred to as dry shrinkage.

About twenty-four samples are placed crosswise in an electric kiln, on supporting bars about 3½ inches on centers. With an oxidizing atmosphere, the temperature is raised at the rate of 100°F., every ten minutes.

Unless special information is desired, the first sample is drawn at 1000°F., and at each 100°F. thereafter. The samples are drawn with a long steel rod and dropped into a pan of asbestos. They will not air-check if the kiln is not allowed to cool before drawing.

When cool, the color, shrinkage, loss of weight, porosity, and specific gravity are determined in the usual manner. The samples are broken, and the strength and texture noted. This information is recorded by curves and figures on the form.

The point at which the sample sags noticeably in the kiln, under its own weight, is designated as the refractory index. A slight softening and stickiness will be noted at from 50 to 100°F., below this point.

The burning range is taken from about the temperature at which the strength reaches a value of 1500 pounds per square inch, up to the point of bending in the kiln

This represents the burning range for extreme classes of ware, and it is not intended to imply that paving brick, for ex-

FIG. 2a

FIG. 2b

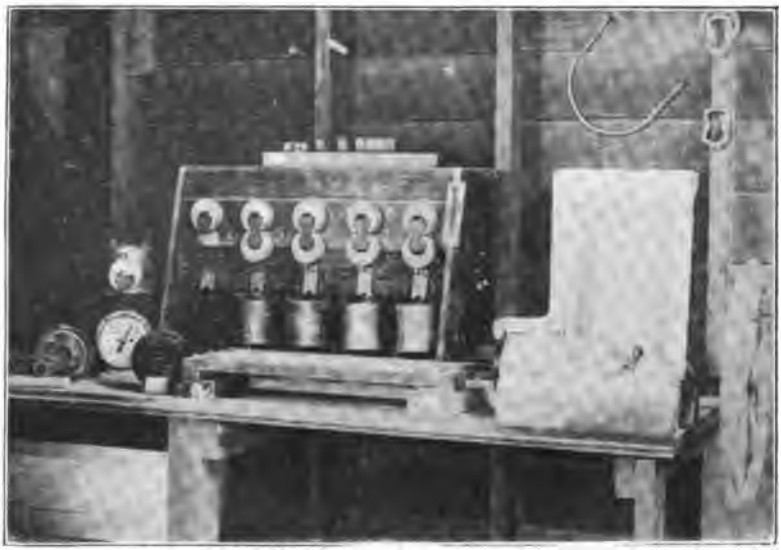


FIG. 3

ample, should be burned to a strength of 1500 pounds, or that refractories should be burned to several thousand pounds per square inch.

Vitrification is represented by a great increase in strength. with a decrease in porosity, and the development of a dense, close, more or less glass-like body. The development of these characteristics is clearly indicated on the test sheet, but no attempt is made to fix any particular point as the point of vitrification.

The original object of these tests was to obtain, in systematic form, such information in regard to clays in actual use for certain purposes, as would enable other similar clays to be recognized and comparison of their properties to be made. The intention was to reduce the procedure to laboratory dimensions, and to assign, so far as possible, numerical values to each of the various important properties of clay. Later, as the system expanded, many other clays, not of direct interest to the original investigation were tested, and their properties noted.

Parallel tests with the small electric kiln and the large yard kilns have been run on a number of different samples. While certain differences are noted, these seem to be small and constant and easily allowed for.

Each of the tests noted has been in actual use over periods ranging from several months to several years, and has given satisfactory results. Upon inspection, it seems possible to determine, with a fair degree of accuracy, the uses to which a clay may be put, or conversely, to determine the limits which ordinarily must not be exceeded, if certain classes of ware are to be manufactured.

The following examples are typical, although it should be understood that these are offered in the nature of suggestions, as sufficient experience has not yet been had to fix definitely the limits of all the various kinds of clay referred to.

The most essential requirement for a fire brick is a satisfactory refractory index. This will vary from 25 to 30. The burned strength at maturity is usually low, from 1000 to 2000 pounds.

FIG. 4.

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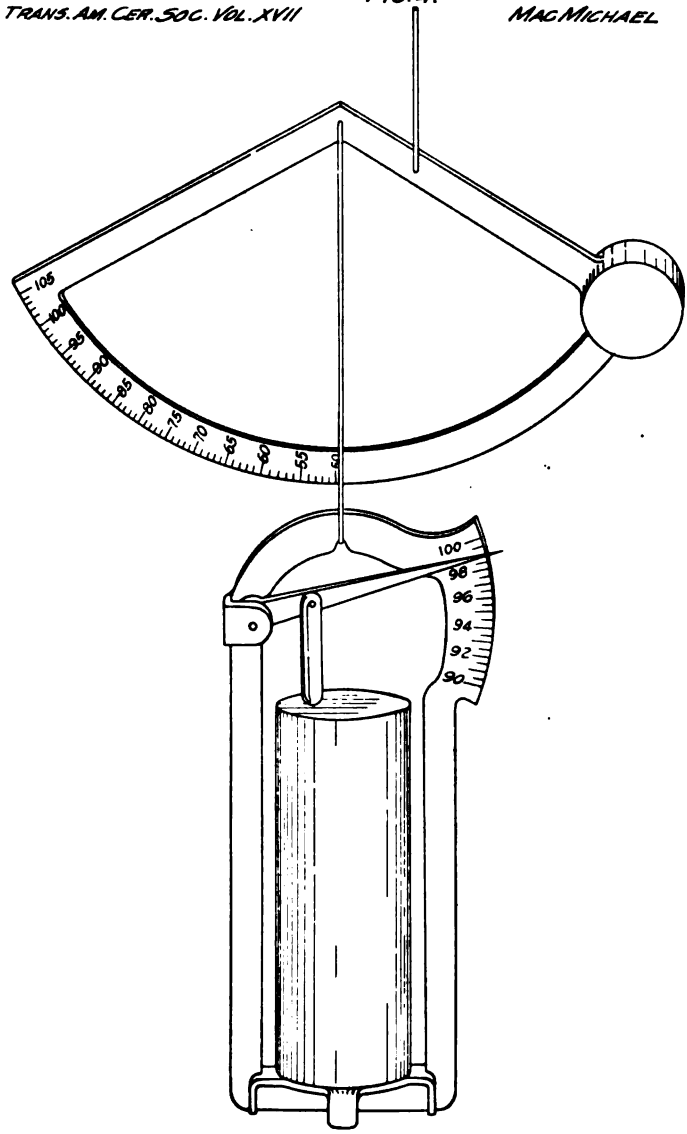


Fire clay, furnace blocks and shapes require sufficient plasticity and dry-strength to permit molding. For this purpose, the plasticity is usually not less than 1.2, representing the number of parts of acidulated water required to form a slip of standard viscosity.

Color is one of the principal characteristics in glazed ware. Usually this must be as light in color as possible, although darker clays are sometimes used, owing to the excellence of other properties, or for practical considerations.

Stoneware clay generally has a plasticity of from 2.0 to 2.5; a wet-strength of from 1.5 to 1.8 pounds per square inch, and a dry-strength of from 250 to 400 pounds. If these limits are much exceeded, serious trouble in manufacture is likely to result.

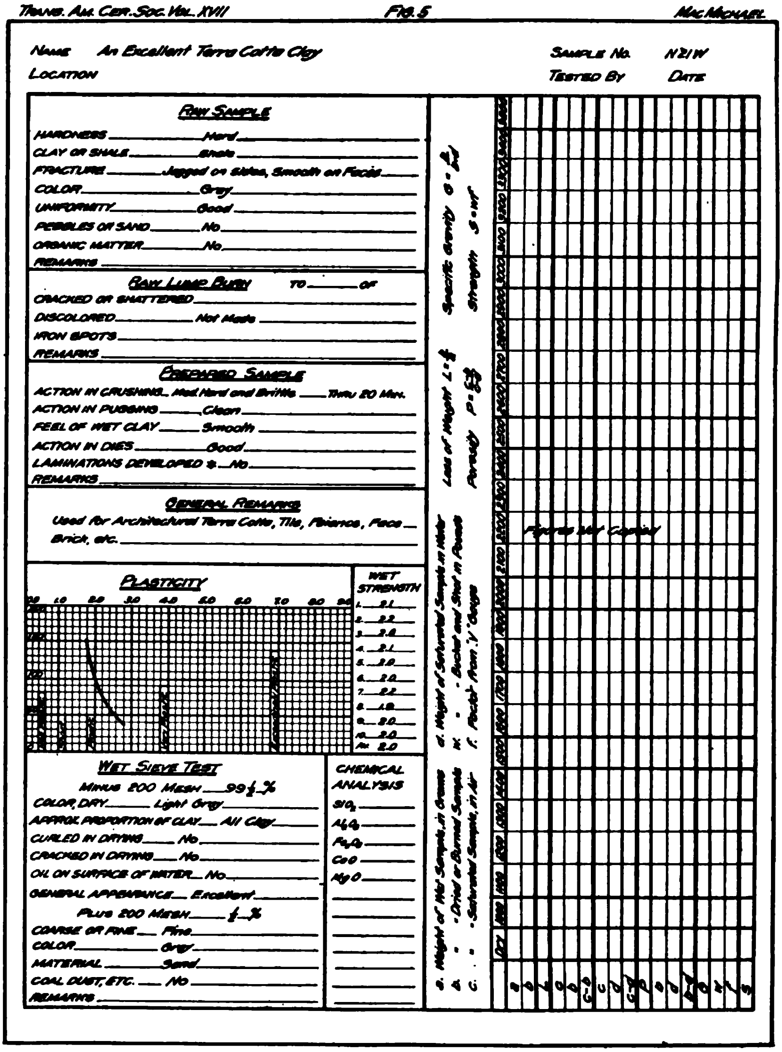
The drying properties must be good. These are closely allied to plasticity, wet and dry-strength, shrinkage, and loss of weight in drying, and should be judged accordingly. The burned-strength at maturity is usually from 2500 to 3500 pounds, with low porosity.

Architectural terra cotta requires a clay very similar to stoneware clay, although grog is ordinarily used in the body. The dry-strength is usually from 250 to 400 pounds and the burned strength at maturity from 2000 to 3000 pounds. While the latter figures represent the general average, the quality of architectural terra cotta does not depend, to any great extent, upon either its strength or its porosity, and it should not be judged by these values. Very refractory clays generally do not glaze well, while a clay burning to good strength and color at low temperatures is usually hard to obtain. A judicious compromise is the usual result.

The requirements for tile and glazed brick depend almost entirely upon the methods to be used in manufacture, and may be judged from the requirements of other similar materials.

The methods for the manufacture of common brick have reached such a stage of perfection in the best practice, that apparently almost any material may be used for this purpose. In general, for any process, the plasticity should neither be excessively high nor excessively low. The burned strength for the

Trans. Am. Cer. Soc. Vol. XVII — Fig. 5 — MacMichael



NAME An Excellent Terra Cotta Clay — SAMPLE NO. N21W

LOCATION — TESTED BY — DATE

RAW SAMPLE

HARDNESS ____ Hard

CLAY OR SHALE ____ Shale

FRACTURE ____ Jagged on Sides, Smooth on Faces

COLOR ____ Gray

UNIFORMITY ____ Good

PEBBLES OR SAND ____ No

ORGANIC MATTER ____ No

REMARKS ____

RAW LUMP BURN TO ____ °F

CRACKED OR SHATTERED ____

DISCOLORED ____ Not Made

IRON SPOTS ____

REMARKS ____

PREPARED SAMPLE

ACTION IN CRUSHING ____ Med. Hard and Brittle ____ Thru 20 Mesh.

ACTION IN PUGGING ____ Clean

FEEL OF WET CLAY ____ Smooth

ACTION IN DIES ____ Good

LAMINATIONS DEVELOPED ____ No

REMARKS ____

GENERAL REMARKS

Used for Architectural Terra Cotta, Tile, Faience, Face Brick, etc.

PLASTICITY

WET STRENGTH

1. 2.1
2. 2.2
3. 2.0
4. 2.1
5. 2.0
6. 2.0
7. 2.2
8. 1.8
9. 2.0
10. 2.0

Av. 2.0

WET SIEVE TEST

MINUS 200 MESH ____ 99½ %

COLOR, DRY ____ Light Gray

APPROX. PROPORTION OF CLAY ____ All Clay

CURLED IN DRYING ____ No

CRACKED IN DRYING ____ No

OIL ON SURFACE OF WATER ____ No

GENERAL APPEARANCE ____ Excellent

PLUS 200 MESH ____ ½ %

COARSE OR FINE ____ Fine

COLOR ____ Gray

MATERIAL ____ Sand

COAL DUST, ETC. ____ No

REMARKS ____

CHEMICAL ANALYSIS

SiO_2 ____

Al_2O_3 ____

Fe_2O_3 ____

CaO ____

MgO ____

a. Weight of Wet Sample in Grams

b. " " Dried or Burned Sample

c. " " Saturated Sample in Air

d. Weight of Saturated Sample in Water

W. " " Bucket and Shot in Pounds

f. Factor from 'V' Gauge

Loss of Weight L = ; Porosity P = ; Specific Gravity G = ; Strength S = wf

Figures Not Copied

better grades has been found to be over 1500 pounds per square inch.

Owing to the greater care used in the manufacture of face brick, these will usually be found to have a burned-strength of not less than 2000 pounds per square inch, with a porosity lower than that of common brick. The color must be pleasing, although a very wide range of colors will be found acceptable to architects and owners. Sufficient work has not yet been done to determine the requirements for working, by any particular method or for securing any particular texture, though this information could probably be obtained by further experiments.

Paving brick require strength and toughness, and the porosity is usually low. The burned-strength of ware tested, was found to be over 4000 pounds per square inch for brick of good quality. These samples seem to have been matured at a point from 1000 to 2000 pounds per square inch below the ultimate maximum strength, which might have been secured. Apparently this margin is required to eliminate sensitiveness in the kiln, and to avoid brittleness in the finished product.

Good sewer-pipe clay showed a plasticity of 1.5 to 2.0; a wet-strength of 1½ to 2 pounds per square inch and a dry-strength of 250 to 400 pounds. It is essential that the clay act well in the dies, though clays with the above numerical characteristics can usually be depended on in this respect. The burned-strength was found to be from 2000 to 3000 pounds. Sewer pipe clay must also take a good salt glaze. This seems to depend somewhat on its chemical properties, especially the amount of iron and low-heat fluxes present. Refractory clays, and clays which do not act well in this respect, can sometimes be made entirely satisfactory by the addition of a suitable amount of dark burning surface clays. This will also often give the finished product a more pleasing color and facilitate marketing.

Structural terra cotta requires clay very similar to sewer-pipe clay, although it does not have to take a salt glaze. Samples tested showed from 2000 to 3000 pounds burned-strength.

Drain tile is ordinarily moderately strong and porous. The working properties are about the same as for sewer-pipe clay.

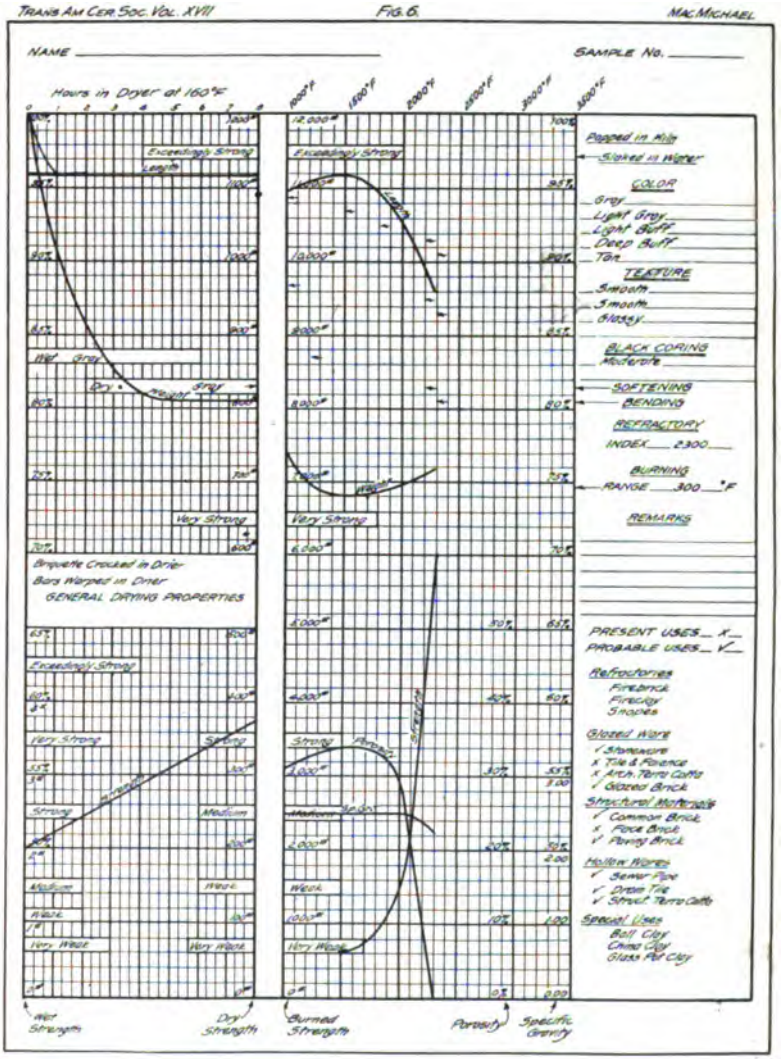

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FIG. 6.
MAC MICHAEL
NAME
SAMPLE No.
Hours in Dryer at 160°F
1800°F
1850°F
2000°F
2050°F
2100°F
2200°F
Exceedingly Strong
Very Strong
Strong
Medium
Weak
Very Weak
Briquette Cracked in Drier
Bars Warped in Drier
GENERAL DRYING PROPERTIES
Dipped in Hcl
Slaked in Water
COLOR
Grey
Light Grey
Light Buff
Deep Buff
Tan
TEXTURE
Smooth
Gritty
Glossy
BLACK CORING
Moderate
SOFTENING
BENDING
REFRACTORY
INDEX 2300
BURNING
RANGE 300 °F
REMARKS
PRESENT USES X
PROBABLE USES V
Refractories
Fire Brick
Fire Clay
Shapes
Glazed Ware
Stoneware
Tile & Faience
Arch. Terra Cotta
Glazed Brick
Structural Materials
Common Brick
Face Brick
Paving Brick
Hollow Wares
Sewer Pipe
Drain Tile
Struct. Terra Cotta
Special Uses
Ball Clay
China Clay
Glass Pot Clay
Wet Strength
Dry Strength
Burned Strength
Porosity
Specific Gravity

The most essential features of a good ball clay are plasticity and color. The plasticity is usually from 4.5 to 6.5. The color should be as light as possible at the finish of the burn. These characteristics are usually associated with a wet-strength of from 2.5 to 3.5 pounds per square inch. The dry-strength is difficult to obtain accurately, owing to the lamination usually present, but it is generally high. The drying characteristics are usually very bad, with cracking, warping, and with large shrinkage both in drying and burning. The refractory index will usually be low, about 22 to 23 with a high burning strength. The plus 200 material of good samples will usually consist of fine gray sand and vegetable matter, about one-half to one per cent in all.

The highest grades of china clay must be white or nearly so when burned. The plasticity will sometimes be as high as 3.5, but the dry-strength and shrinkage are usually low. The plasticity and the loss of weight on drying seem to be an indication of the degree of kaolinization.

Glass-pot and crucible clays require the proper physical characteristics, as outlined above, to permit ease and safety in manufacture, and a moderately strong, dense body to resist the action of fluxes. Glass pots, laboratory crucibles, gas retorts and similar materials do not seem to require as high a refractory index as might be expected.

An important function of clay testing is to give warning of any variation in the raw materials supplied to the factory. In the testing of these materials, any variations of consequence can usually be noted quite readily. If accurate numerical data are available, showing the nature and the amount of the variation, the necessary changes can usually be made promptly.

In trying out new lots of flint and feldspar, parallel tests are run on the regular mixtures, using the old material and the new, and the results obtained are compared with each other and with previous records. By these and similar methods the danger of loss from unintentional variations in any of the ingredients is practically eliminated.

FIG. 7

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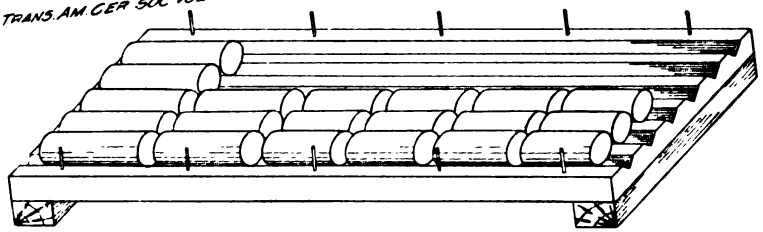
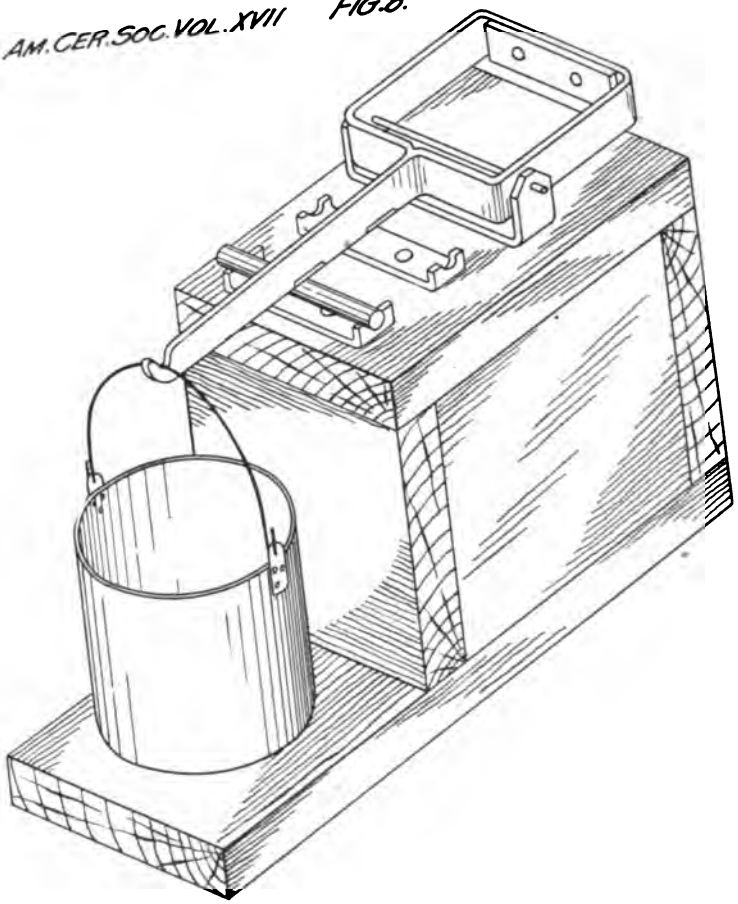


MAC MICHAEL

FIG. 8.

TRANS. AM. CER. SOC. VOL. XVII



The proper amount of deflocculating agent, such as sodium carbonate, to be added to a casting body, may be determined with great rapidity and accuracy, by means of the viscosimeter. As the requirements seem to vary considerably from time to time, especially where precipitated whiting is used in the body, it seems important that this matter be frequently checked in order to secure the best results.

For best results in glazing, the specific gravity and the viscosity of slips and glazes should be held constant. At one plant these materials are ground as a denser slip than is desired for use and later reduced to the proper specific gravity with water. The viscosity is then adjusted by means of the viscosimeter, using hydrochloric acid or sodium carbonate as required. A very marked improvement in the quality and uniformity of the glazed ware was apparent after this system had been installed.

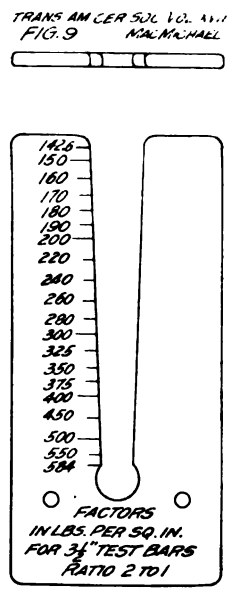
The strength test, as an indication of the degree of vitrification, is very much more sensitive and accurate than any other test known to the writer. This indication ordinarily is noticeable hundreds of degrees before any other material change is noted, except that of color. With some clays a very marked increase in strength is noted as much as 800°F. below any marked change in porosity.

It frequently happens that a clay, not suitable in itself for a given purpose, may be mixed with other clays, or with sand or grog to develop the desired properties. For example, a stoneware or terra cotta clay with excessive plasticity, may be reduced by mixing with a shorter clay, or with sand or grog. The properties of the mixture are then determined as on a simple clay.

In order to determine in advance the effect of such mixing, it is necessary to know the law governing mixtures. This may be stated as follows: The properties of mixtures of clays are approximately straight line functions of their individual properties and proportions. For example, if a clay with a plasticity of four be mixed in equal parts with a grog, having a plasticity of zero, the plasticity of the mixture will be approximately two

Or if the burned strength of a clay at a given temperature is 3000 pounds per square inch, and it is mixed with a grog, having a zero strength at any point below the maturing temperature, the burned-strength of the mixture will be approximately 1500 pounds per square iuch.

While in the nature of the case such figures cannot be expected to be exact, they will be found helpful in making preliminary estimates.



The temperature to which a clay should be burned is obviously the lowest at which the desired properties may be secured. The numerical value of these properties can frequently be fixed in advance, and the clay manipulated to secure the results in the most economical manner.

For example, if 2000 pounds is determined as being the proper strength for a certain class of ware, this strength may be obtained with straight clay at say 2000°F. With grog, it may be necessary to go to 2100°, while if mixed with a less re-

fractory clay it may be possible to carry the kilns only to 1900°F. without in any way injuring the value or the appearance of the finished product. As a kiln moves very slowly in going over the peak of the curve and as the wear and tear on a kiln itself increases very rapidly at high temperatures, the savings to be effected in fuel, and repairs, and in time of burning, may be much larger than would appear at first glance.

In conclusion, it would seem that for a given class of ware, the desired numerical values should be determined in advance, if this be practical, and the raw material manipulated to secure these results in the most economical manner.

Having determined the materials and methods apparently most suitable, continuous checks should be maintained on the sources of raw material and on factory processes. A very large part of this work, both of the preliminary investigation and of the maintenance of checks and permanent records, can be done rapidly and economically in a properly equipped laboratory. The expense of the equipment and operation of such a laboratory, is usually very slight as compared with the practical commercial value of the results to be obtained.

DISCUSSION

Mr. Bleininger: I was very much interested in the paper but it seems to me that owing to the large mass of material presented it will be impossible to take the time to go over the very many points that have been covered. I think Mr. MacMichael deserves the thanks of all of us for having presented in a comprehensive manner such testing methods as are available or can be made available at almost every clay-plant. Personally I do not agree with all the points made, of course and Mr. MacMichael does not expect me to do so. I am very much gratified and pleased also with the result he has obtained with the viscosity apparatus. I know a number of the members of this Society have twitted me occasionally about the viscosity bug I developed about eight years ago, and they thought I was trying to advocate a very theoretical sort of an instrument. I was also

interested in knowing that he has worked out the Conette viscosity apparatus invented by a French physicist which in modern colloidal chemistry has proved effective and accurate. We have a viscosity apparatus at our laboratory which is too complicated for general work; it cost about $500; its accuracy is very excellent, it is capable of giving us viscosity expressed in absolute units, but as I said before, its general application is not practical on account of the cost. We are having designed at the present time an apparatus on the same principle Mr. MacMichael has shown, only it is supposed to be run at lower velocities, and its accuracy is increased by attaching to the wire a mirror so that the deflection may be read from a scale. In obtaining viscosity by means of the present apparatus, the relative viscosity is obtained not only from the deflection but rather by the deflection multiplied by the time (in seconds) per revolution. Also, I am not in favor of using the electric furnace for test burns, and I would also object to the rapid rate of firing employed.

Mr. MacMichael: If you will permit me just another word, there is one point in regard to these test sheets that I did not bring out very clearly, and that is the value of having in uniform style all the information that is ordinarily of interest. We found in our early experiences that we tested clay and would think we had everything we wanted to know about that particular clay, yet about six months later we would have given a day's work to have some other information that was not available, because our original test was not complete. We found by experience that when we tested clay it is much more satisfactory to put down all the information.

DIRECTIONS FOR CLAY TESTING

1. A raw sample of about ten pounds weight is required.
2. Note characteristics as indicated on form under raw sample.
3. Dry and place in a two gallon jar.
4. Crush six pounds, dry weight.

5. Grind through 20 mesh screen for plastic clays and 40 mesh screen for shales.

6. Note how clay acted in crushing and drying.

7. Place in wet pan and mix thoroughly while dry to insure uniformity.

8. Remove 800 grams for wet-sieve and plasticity tests.

9. Pug sample remaining in wet pan to proper consistency.

10. Note how the clay acted in pugging.

11. Hard clays and shales should be aged 24 hours. Soft clays usually require no aging.

12. Into a bottle containing 600 cc. of water, pour slowly a weighed quantity of dry, ground clay, the amount to be estimated from the probable plasticity of the clay; from 600 grams for extremely short clays to 100 grams for ball clays.

13. Blunge in an electric stirring machine until thoroughly dissolved, which takes from 1 to 24 hours.

14. Place 100 cc. of slip in the viscosimeter and note viscosity recording the point on the extreme right hand line of the form.

15. Add HCl one drop at a time, to the slip in the viscosimeter and stir, noting the values obtained, until a maximum value for plasticity is reached and the curve starts to fall. Record from right to left as indicated on form. If maximum point of curve falls below 100°V., the slip is too thin, and the entire test must be repeated using less water.

16. When maximum acid viscosity has been reached (usually with the addition of from 5 to 20 drops HCl) record in the body of the form under proper column. Thus, 1 part by weight of water added to dry clay forms a 100 percent mixture to be recorded in column 1. Four parts by weight of water form 400 percent mixture to be recorded in column 4, etc.

17. Add weighed quantity of water to the slip to reduce to the next higher percent in even hundreds and record the viscosity. Thus, 300 grams of 200 percent slip contain 100 grams of dry clay and 200 grams of water. Adding 100 grams of water reduces this to a 300 percent slip. Repeat as often as necessary to obtain length of curve desired, and plot curve.

18. The numerical value of the plasticity of a clay, is the weight of water added to the clay, which, when blunged and acidulated to a maximum value with HCl, will produce a slip of 100° viscosity.

19. Record numerical value of plasticity in proper place on form.

20. Clean viscosimeter and pour in 100 cc. of fresh slip from the blunger. Add Na_2CO_3 drop by drop, recording results as shown on the form.

21. Place 100 grams of dry ground clay in about 300 cc. of water in blunger. Stir until thoroughly dissolved. (Put water into bottle first.)

22. When thoroughly dissolved, pour contents of bottle on to the 200 mesh screen in the wet sieve machine, using plenty of water to wash out the bottle. Plus 200 mesh material is caught on the screen. Minus 200 material passes through into the one-half gallon milk crock below.

23. Wash the material remaining on the screen into a bowl under a small stream of water from the faucet. This plus 200 material should consist of fine sand mica, etc. without clay particles, which can be crushed between the fingers. Water running off should be clear. Place in the drier.

24. Place the minus 200 material in the drier.

25. If the clay has been aged, re-pug to proper consistency.

26. Work by hand into solid mass and place in a cylinder press.

27. Attach figure 8 die, and run out a 12 or 14 inch length of clay. Die should be clean and bright inside and wet before using. Cut into one inch lengths with gang cutter.

28. Make wet strength test on ten samples, taking the weight of the bucket, sand, clamp and lower half of the sample in pounds. Recover clean samples which remain in the upper clamp, wasting the sanded sample which falls into the bucket. Record weights on form.

29. Attach ½ inch die and fill one V-rack with samples.

30. With wire cutter, notch one-half inch samples about one-fourth way through with a sliding stroke, in front of each pair of

guide posts, making 32 samples one-half inch by five inches. The samples should lie straight and true in the bottom of the grooves.

31. Remove one string of four samples and weigh, recording average weight of one sample as wet weight "*a*" on the form. Surplus clay should be removed from ends of string before weighing.

32. Note color of wet clay.

33. Note how clay acted in the die.

34. Mark sample number with stencil about 1½ in. from left end of samples.

35. Loosen samples slightly with fingers to prevent sticking.

36. Notch samples lightly with 100 mm. gauge.

37. Place rack and samples in drier.

38. Press 100 grams of wet clay in a briquette mold. Stamp the sample number on briquette.

39. Place briquette in test drier. Thermometer should stand at 160°F. and clock at 12 M. Record loss of weight and shrinkage every ten minutes, plotting curve on form.

40. When 5 in. samples are thoroughly dry, remove from drier on rack.

41. Note if the samples have warped in the drier.

42. Break the samples carefully at 5 in. notches. Only the straightest and most perfect should be put in the kiln, others being reserved for dry-strength test.

43. Place 27 samples in an electric kiln on supporting racks. Samples should not touch sides or bottom of kiln. Place numbered end to left side of kiln.

44. Burn kiln slowly at first, until samples are thoroughly heated through; afterwards at the rate of 100° rise each ten minutes.

45. Extremely fine grain clays may pop in kiln. In this ease, they must be heated very slowly until red heat is reached.

46. When 1000°F. is reached, remove one sample and drop into a panful of asbestos. At each succeeding 100° draw an additional sample. Mark samples on right end when cool with lead pencil, and place on rack with the dry samples.

47. When bars in the kiln soften and stick slightly, the burn is nearly complete. When bars bend under their own weight, the burn is complete, and the power is shut off.

48. Record length in mm. of each sample including dry bars plotting curve direct.

49. Record color of dry and burned samples.

50. Record dry or burned weight of samples under "*b*" on form.

51. Soak burned samples in water five or six hours, nearly submerged.

52. Weigh samples submerged in water and record as "*d*."

53. Roll samples on dry towel to remove surplus water.

54. Weigh in air and record as "*c*."

55. Break dry and burned samples in the bar machine, and weigh the bucket and shot. Record as "*w*." The average of several dry bars should be taken.

56. Place broken bar in "V" gauge and read factor opposite the center of bar. Record as "*f*".

57. Note amount and point at which black coring disappears, if present at all.

58. Note texture of break in burned samples.

59. Note if lamination or piping has been produced in die as shown by broken sample.

60. When water is entirely evaporated, remove bowl from drier. Note cracking, curling, etc., as indicated on form.

61. Note character and weight of plus 200 and record as indicated on form.

62. Make necessary calculations from above data and plot curves for length, weight, porosity, specific gravity, strength, etc. Record miscellaneous data as indicated on form.

63. If chemical analysis is determined, record on form.

64. Note burning range from temperature at which 1500 pound strength is developed up to bending point.

65. The temperature at which bending occurs is recorded as the refractory index, dropping two ciphers.

66. Place samples and record in permanent file for future reference.

STRENGTH TESTS OF OREGON BUILDING BRICK

BY IRA A. WILLIAMS

Under the writer's direction, the Oregon Bureau of Mines and Geology has in the past year made a series of tests of building brick from Oregon factories. The standard tests of American Society for Testing Materials for cross-breaking, crushing and absorption were made with minor departures only in method. Twenty-nine firms furnished samples for testing, fifteen of which made stiff-mud brick, thirteen made soft-mud, and one dry-press brick. All told, thirty-six sets of samples of five brick each were tested, a total of 180 brick.

The collecting of the test brick was done by the writer, or under his explicit instructions, a careful effort being made to select in each case representatives of the average best output of the kiln or yard. The chief purpose of the tests was to secure specific data on each product, for the use of the manufacturer in marketing his ware or submitting it in contractual competition, and for the user of brick who must obtain a material possessing certain qualities and decide among competing bids. The sample bricks for testing should, therefore, stand for such a portion of the output of the plant as the maker could furnish in quantity, in order that the results of the tests might be of full value to both maker and user. In the case of plants that put upon the market more than one distinct grade or variety, separate sets of average quality were selected from each market class. In the tables, each plant is given a number ("Set No.") the accompanying small letters referring to separate grades or classes of product.

A somewhat detailed discussion of these results has recently been given in the *"Mineral Resources of Oregon,"* (Vol. 1, No. 7), published by the Oregon Bureau of Mines and Geology, Corvallis, Oregon. It is the purpose of this brief paper, after presenting the separate results for each set of brick tested, to call attention to certain interesting relationships in the results ob-

tained in the strength tests, beyond those of which specific mention has been made in the publication referred to.

Figure 1 shows graphically by means of straight lines the relation existing between the maximum and minimum crushing strengths and the average, also the relation between the greatest and least moduli of rupture and the average for each set of five bricks tested. In each instance the co-ordinate positions of the dots at the ends of a line mark the extremes of both moduli and

TABLE I—TESTS OF OREGON SOFT-MUD BUILDING BRICK

SET NO.	WATER ABSORBED	MODULUS OF RUPTURE (lbs. per sq. inch)			COMPRESSIVE STRENGTH (lbs. per sq. inch)					
					TESTED DRY			TESTED WET		
		MAX.	MIN.	AV. OF FIVE BRICK	MAX.	MIN.	AV. OF FIVE BRICK	MAX.	MIN.	AV. OF FIVE BRICK
	percent									
5	25.0	408	302	355	1820	1530	1718	1726	1110	1508
7	22.9	623	252	494	2360	1930	2122	3220	1800	2393
9	29 5	243	170	207	1235	1073	1144	1390	1007	1151
10	49.6	457	279	360	1430	923	1255	1760	1238	1407
16	26.9	754	281	498	2730	1261	1946	3470	1710	2305
17	21.6	715	185	490	4970	1210	2868	5080	1150	3113
22a	18.2	806	599	699	3030	2442	2761	3195	2310	2749
22b	17.4	818	663	732	2966	2361	2702	2650	1970	2263
23	22.5	354	198	242	1543	997	1186	1356	939	1152
24	21.3	398	184	295	1733	720	1467	1740	718	1374
26	20.8	440	248	334	2185	1608	1851	2070	1230	1702
27	19.4	910	559	727	2966	2328	2581	2770	2241	2450
28	19.8	679	293	515	3818	1872	2772	3378	1680	2571
29	21.7	927	612	699	4180	3010	3524	4140	2778	3327

compressive strength, and the circle indicates the average result of the set. Each composite line marked "A" (also made heavier) stands for a set of stiff-mud brick; those with no index capital letter, for the soft-mud results. The numerals correspond to the "Set No." in the tables. Only a part of the results compiled are plotted in Fig. 1.

It will be noted that the soft-mud lines are prevailingly shorter and probably a little more nearly parallel in direction

than those representing the stiff-mud brick; also that they tend to group themselves rather closely at the lower left in the region of both lower cross-breaking and lower compressive strengths. The stiff-mud lines are not only more scattered, showing a wider range of strength, but the distance between extremes in each

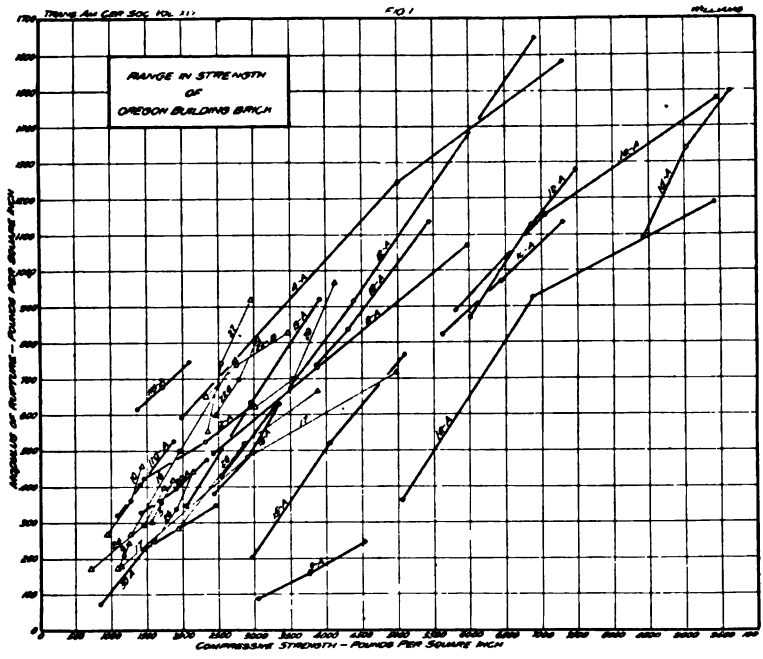
TABLE II—TESTS OF OREGON STIFF-MUD BUILDING BRICK

SET NO.	WATER ABSORBED	MODULUS OF RUPTURE (lbs. per sq. inch)			COMPRESSIVE STRENGTH (lbs. per sq. inch)					
					TESTED DRY			TESTED WET		
		MAX.	MIN.	AV. OF FIVE BRICK	MAX.	MIN.	AV. OF FIVE BRICK	MAX.	MIN.	AV. OF FIVE BRICK
	percent									
1a	12.8	1195	368	921	9400	5080	6840	9480	5010	6414
1b	9.5	1280	870	1118	7490	6010	6868	8550	5880	6856
1c	16.6	1137	827	988	7280	5630	6470	7900	6590	7268
1d	13.7	1500	1088	1340	9680	8460	9038	9820	7900	8670
1e	14.0	1484	894	1160	9440	5770	7036	7920	4110	5470
2	20.7	612	421	522	2910	1450	2296	3530	1862	2844
3	21.6	246	93	163	4570	3050	3768	4010	2760	3282
4	28.7	1590	598	1241	7280	1990	5014	7790	2030	4858
6	20.9	772	444	598	3480	1890	1998	3630	1740	2608
8	17.5	1074	495	735	5940	2410	3780	3960	2280	3042
11a	20.0	523	323	406	1790	1135	1386	1710	1164	1429
11b	20.4	748	613	668	2125	1384	1740	1907	1450	1651
12	18.8	1647	435	907	6880	2590	4376	5420	2544	3836
13	21.9	920	354	621	3880	2080	2927	4430	1744	3012
15	15.4	763	202	518	5140	2940	4078	6050	2980	4340
18	17.7	617	392	488	3340	2440	2818	3240	2470	2765
19	15.8	1130	740	839	5470	3770	4264	5420	3450	4362
20	25.1	483	315	397	2302	1400	1814	2045	1370	1811
21	19.9	962	735	832	4670	3580	4152	4830	3540	3988
30	25.4	366	73	232	2486	831	1432	2290	968	1497

test is in general greater than is shown for the soft-mud brick. From the tables, it will be seen that, as a rule, the brick showing the lower strengths have a higher percentage of absorption.

It should be particularly noticed that in Fig. 1 the lines for the soft mud bricks are comparatively short. Since these lines are nearly parallel, it means that there are no great extremes

in strength, expressed on either the vertical or horizontal component. A wide or a narrow range between maxima and minima on sets, of which the individual brick are selected as being fairly uniform in character, may mean one or more of several things. So far as the tests show, there is without question a correspondingly wide or narrow range in the strength qualities of the individual samples. Such variations in range may indicate careless-



ness in choosing specimens for testing, or inability on the part of the person making the selections to distinguish in all cases between brick of considerable difference in quality. Inasmuch, however, as this range in results is noticeably less for the group of soft-mud brick, as against the group of stiff-mud, it would appear that the type of brick and its method of manufacture have something to do with the possibility of selecting specimens

of uniform quality. This, in the writer's opinion, is the principal cause of the variations noted.

Stiff-mud brick are frequently quite difficult to judge by mere hand inspection, even by those with considerable experience. This is largely due to the skin produced by the die, to the range in the hardness of burning usually found in an enclosed kiln of stiff-mud brick, and more particularly because of the disguising effect produced by frequent changes in the character of the kiln atmosphere during burning. In other words, the density or hardness, and interior texture and structure, are not always evident to the eye, or disclosed by the ring of the brick when tapped, one against another. With the soft-mud product, the conditions are somewhat different. These are generally burned in open or clamp kilns, in which the fires are under much less accurate control. They are subjected progressively to the conditions of rising heat without many alternations from oxidizing to reducing conditions or vice versa, or of sufficient duration to produce permanent surface effects on the brick. Soft-mud brick are, therefore, more likely to show their character on inspection and can be more truly judged "by hand" than stiff-mud brick. This fact is not only brought out by the results of this particular investigation, but I believe is a matter of experience to all who have had occasion to choose representative brick for any purpose whatsoever.

The effect of moisture on the strength of brick is a question that has received some attention and discussion in the past few years. The actual value of ascertaining to what extent strength is affected by saturating the brick, is believed to be open to question, since, saturated or dry, acceptable brick for all ordinary purposes possess, as a rule, many times the compressive resistance necessary to carry the weight put upon them in use. Moreover, for a standard test, a condition of complete dryness can be much more readily and definitely brought about and maintained than can saturation, principally for the reason that no two brick absorb alike, and the point when absorption ceases (whether the pores are completely filled or not) is difficult to ascertain. Further, mere presence of water in the pores of a

brick is not a condition affecting its strength to any known extent, unless the compressive resistance of the water itself in such a position be considered, when, in case portions of it could not flow, it would have a tendency to support or strengthen the structure of the brick. It is, however, the effect of this water upon the solid portions of the brick, the cell or pore walls so to speak, that determines whatever influence will be exerted on the strength of the brick. In a well-burned brick, reasoning *a priori*, it would not be thought that the mere inclusion of water could have an appreciable effect, within any reasonable length of time, upon its strength. Upon the soft-burned or medium-burned brick however, the probability appears to be that, if anything, a weakening would result. Followed to a limit, the very extreme of this condition is, of course, the unburned brick, which moisture promptly melts to shapelessness. For application to various brick from various yards, there could, therefore, be no certainty whatever in the assumption of a period of saturation before testing, such that the structure of all susceptible brick would be affected by water in a proportionate degree or, from the practical standpoint, to any such extent as it might be in very little or much longer time after laying in the wall. Owing to this indefiniteness which must ever enter into the devising of ways and means for applying the wet test, and of the equally more definite test dry, besides at the very outset the low practical value of compression as a strength test, there appear no ample reasons for seriously devoting much attention to the wet crushing test of building brick. As much cannot, however, be said with reference to the cross-breaking test.

The crushing test of the Oregon brick was made on both the wet and the dry samples. One-half of each of the five brick in a set were crushed dry and the remaining half after immersion in water and boiling for four hours. Inspection of the tables of results will show that in five out of the fourteen soft-mud tests the average crushing strength was slightly higher for the wet than the dry. In the stiff-mud, eight out of the twenty sets give barely higher average figures in the wet than in the dry tests. The difference is rarely greater than might be expected in test-

ing the two halves of individual brick under the same conditions either dry or saturated. On the other hand, among the remaining sets in which the average results of the dry test are higher, the differences are no larger, it is believed, except in a few instances, than one would be warranted in ascribing to expected variation in halves of brick and manipulation errors.

Oregon Bureau of Mines
and Geology.

THE INFLUENCE OF SOME UNUSUAL ZINC COMPOUNDS IN A CHROME GREEN GLAZE

BY R. H. MINTON

As the conclusion to his article on Chromium Oxide in Glazes Containing Zinc, Vol. X, p. 131, M. L. Bryan states, "that the zinc oxide acts as an agent, supplying the oxygen necessary to change the Cr_2O_3 to a higher form, where it remains as such, unless it is given a violent reducing atmosphere."

"The coloring power of chromium then is merely a question of oxidation, and when zinc is present the chromium is oxidized to its higher form, hence the brown color."

In Vol. XV, p. 123, A. R. Heubach in discussing the formation of various zinc-chromium colors states it as his belief "that it is merely a question of oxidation."

In Vol. XVI, p. 261, the writer stated that, "there can be no question but that oxidation plays the leading part in the action of chrome, in glazes containing zinc."

Further consideration of the question led to the conclusion that while oxidation and reduction have considerable bearing upon the formation of chromium browns in the presence of zinc, it is not due to the formation of higher forms of chromium through the oxidation by zinc oxide, but by the formation of zinc chromates, which are, however, apparently influenced by kiln conditions.

If these brown and tans are due to oxidation of the Cr_2O_3 by the zinc oxide, the introduction of the zinc into the glaze in forms containing no oxygen should throw light upon this theory.

Accordingly a series of trials was arranged by which various forms of zinc would be introduced in equal equivalents in a glaze, and to all of which equal percentages of Cr_2O_3 would be added.

If the chromium colors other than green are due to the formation of zinc chromates, all in the series should produce shades on the order of tan, brown or kindred colors, while if these shades

are due to oxidation by the oxygen from the ZnO those glazes in which zinc salts containing no oxygen were introduced should at least show evidences of greens.

The glaze selected for this experiment was,

$$\left.\begin{matrix}.30\ K_2O \\ .40\ CaO \\ .30\ ZnO\end{matrix}\right\} .70\ Al_2O_3 . 2.60\ SiO_2$$

containing 1½ percent Cr_2O_3.

BATCH WEIGHTS

167.1 Maine spar.
40.0 Whiting.
103.2 China clay.
X Zinc salt.
Y Cr_2O_3.

The various zinc salts used were the Baker's Analyzed Chemicals, which are about as pure as can be procured. These compounds are not absolutely pure, nearly all contain very minute quantities of impurities, which are not likely, however, to exert the slightest influence upon the effects produced in this experiment.

It is not necessary to give the analyses of these zinc salts. The chromium added was in the form of Cr_2O_3, except in glaze No. 356 to which none was added.

Table I gives the glaze numbers, together with the zinc salts used to introduce the zinc content, their formulas and equivalent weights, and the weight used for the batch.

The glazes were made up in batch weights in grams, and ground in a small ball mill for ten hours. Each glaze was made up with sufficient high grade glue to form a stiff jelly and then painted on the trials with a brush. Six heavy coats were applied over a white underslip, which had also been glued so that when dry it was very hard. The trials were an ordinary terra-cotta grog body made into tiles 4½ in. by 3 in. by ¾ in.

The first set were burned in a large muffle kiln, fired with bituminous coal, requiring 138 hours to reach cone 8 and cooling in about 144 hours. Oxidizing conditions prevail most of the time, except possibly toward the finish.

TABLE I

GLAZE NO.	ZINC SALT USED	FORMULA	EQUIV. WEIGHT	WEIGHT USED
350	Metal	Zn	65.37	19.61
351	Acetate	$Zn(C_2H_3O_2)_2+3\ H_2O$	237.47	71.24
352	Borate	ZnB_4O_7	221.37	66.41
353	Bromide	$ZnBr_2$	225.21	67.56
354	Carbonate	$ZnCO_3$	125.37	36.61
355	Chloride	$ZnCl_2$	136.29	40.88
356	Chromate	$ZnCrO_4+7\ H_2O$	307.48	92.24
357	Hydroxide	ZnO_2H_2	99.38	29.81
358	Nitrate	$Zn(NO_3)_2$	189.42	56.83
359	Oxalate	$ZnC_2O_4+2\ H_2O$	189.40	56.82
360	Oxide	ZnO	81.37	24.41
361	Peroxide	ZnO_2	97.37	29.21
362	Phosphate	$Zn_3(PO_4)_2+4\ H_2O$	152.75	45.82
363	Sulphate	$ZnSO_4$	161.44	48.43
364	Sulphide	ZnS	97.44	29.83
365	Barium	$BaCO_3$	197.00	59.10

Results from Kiln. No. 350—Nearly a flesh color. Surface full of smooth bubbles like smallpox marks. Seems to be over-fired.

No. 351—Light salmon-tan color. No bubbles. Surface slightly shiny.

No. 352—Strong purplish pink. Full of smooth crate-like holes.

No. 353—Almost identical with No. 351 in color and texture.

No. 354—Exactly like No. 350 in every way.

No. 355—Considerably more pinkish than No. 350. Full of smooth bubbles.

No. 356. Very dark, strong reddish color. Covered with very fine bubbles.

No. 357—Nearly like No. 350, with slight purple shade. Surface bubbled.

No. 358—Pinkish tan color. Surface full of bubbles.

No. 359—Almost the same as No. 358 in every way.

No. 360—Identical with No. 350 in color and texture.

No. 361—Light tan. Surface full of smooth holes.

No. 362—Very decidedly pink. Surface glossy and with some fine bubbles.

No. 363. Pinkish tan. Well matured glaze. Quite glossy. No bubbles.

No. 364—Same as No. 350 for color. Bubbles very minute.

No. 365—Dark dirty green. Very fine mat surface.

Summary. 1st. No evidence of green color in any glaze containing zinc from any source.

2nd. Zinc chromate produces strongest color.

3rd. Zinc phosphate produces the strongest pink shade.

4th. Most of these salts have not produced good glaze texture.

5th. Zinc salts not containing oxygen destroy the green color of Cr_2O_3 the same as zinc salts combined with oxygen.

Conclusions. 1st. Color or shade produced is influenced by the form of zinc used.

2nd. Chromium oxide in the presence of zinc produces colors other than green, through the formation of zinc chromates rather than through the oxidation of the Cr_2O_3 to higher forms.

In order to determine the effect of different firing conditions, another set of these trials was placed in a small muffle test kiln, ample space being provided around the trials. This burn was made in 39 hours, cone 8 going flat; and the cooling took place in 36 hours.

Results from Short Burn. No. 350—Drab, with pinkish cast. Good mat texture, with slight sheen.

No. 351—Slightly more brown than tan, otherwise same as from long burn.

No. 352—Purplish pink. Surface full of large smooth bubbles.

No. 353—Same as No. 351 above.

No. 354—Pinkish tint showing through faint green cast on surface.

No. 355—Tan. Surface smooth and free from bubbles.

No. 356—Darker than from long fire and not so reddish. Good texture.

No. 357—Considerably lighter shade of No. 350. Good surface.

No. 358—Tan with drab tint. Texture good. No bubbles.

No. 359—Same as No. 358. Very different than from long burn.

No. 360—Same as No. 358. Very different than from long burn.

No. 361—Darker tan than No. 355. Texture good.

No. 362—Very fine pink. Matures well and very glossy.

No. 363—Slightly more pinkish than No. 355.

No. 364—About same as No. 350, somewhat lighter shade.

No. 365—Fine moss green, running to brownish green on edges where thin.

Summary. 1st. Short fire has made much difference in maturity. Number 350 is the only one not having good surface.

2nd. The short fire shows influence upon most of the colors. More tendency to show influence of green in tints.

Conclusion. The results of the short fire have only confirmed that reached from the first burn, namely, that the colors produced from Cr_2O_3 in the presence of zinc in glazes is not due to oxidation by ZnO but to production of zinc chromates. The shades of the zinc chromates are probably influenced by the kiln conditions to some extent.

Particular attention is called to the fine pink of No. 362, by the use of the phosphate of zinc.

STUDY OF THE MOST FUSIBLE MIXTURES OF K_2O-CaO-Al_2O_3-SiO_2 [1]

BY HAROLD H. HANNA

This study is one of a large number dealing with silicates and their deformation behavior in reference to the commercial materials used by clayworkers, *i e.*, feldspar, whiting, kaolin and quartz. The work of Dr. Seger gave to us, what he thought to be the most fusible mixture of the oxides here studied. The modern investigations of melting points by the geophysicists of both Europe and the United States have indicated that a fruitful method of investigation exists in the study of eutectic mixtures. Following this suggestion, the study here presented was undertaken. The minerals employed as a source of the various oxides have been chosen with the object of duplicating as nearly as possible the materials with which Dr. Seger worked. Any success attending this study will prove especially valuable to ceramic science in aiding in the development of easily fusible glazes without resorting to the use of volatile or soluble constituents, or to the fritting of the materials before their employment as glaze ingredients. Also, favorable results should be valuable in lowering the temperature at which Fe_2O_3 must be introduced into pyrometric cones, and since all oxides of iron are extremely sensitive to kiln atmospheres, this would itself justify the investigation.

Briefly stated, the general method of attack was by means of the development of deformation eutectics. All the data available on this subject was consulted and made use of where possible, after first checking up.

According to the light of present day knowledge, fusion in a silicate mixture is due to the formation of a fluid eutectic and the solution of the remaining solid material in this eutectic. Therefore, by a selection of the eutectics with the lowest deformation temperatures and their proper blending, we may hope to

[1] Thesis, Ohio State University, 1915.

secure maximum fluidity or the mixture with the lowest deformation temperature.

References. Seger, Vol. I, p. 224-249. Measurement of high temperatures. In order to develop a suitable method which would give an indication of the heat treatment of ware in a kiln, Dr. Seger aimed to work out a series of mixtures which would melt at fairly regular temperature intervals. To do this, he first determined the most fusible mixture of the materials he decided to make use of, *i e.*, whiting, potash feldspar, kaolin and quartz. Since the chemical composition of commercial materials vary and in order to make results of different investigators comparable, the chemical analyses of materials used should be given. The following are analyses of the ingredients used by Dr. Seger:

TABLE I

	BECKER FELDSPAR	ZETTLITZ KAOLIN	NORWEGIAN QUARTZ	CARRARA MARBLE
Silica	64.32	46.87	98.52	1.00
Alumina	19.41	38.56	1.04	0.12
Iron oxide	0.14	0.83	0.01	
Lime	trace	trace	.....	54.93
Magnesia	0.35	trace	.....	0.21
Potash	12.90	1.06	0.40	.....
Soda	2.10			
Ignition loss	0.57	12.73	.....	.....
Carbon dioxide	.....	.....	.....	43.76
	99.74	100.05	100.00	100.02

His general method of procedure was, first, to add to the feldspar separately, calcium carbonate, kaolin, and quartz. He found in each case, that these mixtures were more infusible than the feldspar alone. He then mixed the four in different proportions and he obtained a lowering of the deformation point. From this study he concluded that the most fusible glazes were neither those high in alumina nor those lowest, nor those with the highest content of alkali, but that there seemed to be a definite ratio between the alumina and the fluxes. He then prepared a number of series increasing the silica in one series and keep-

ing the R O constant (0.2 K_2O 0.8 CaO) throughout; and in another series holding the silica constant and varying the alumina. From this study, he found that maximum fusibility was reached with 0.5 equivalents Al_2O_3. The formula of the mixture fusing first was:

$$\left.\begin{matrix}0.20\ K_2O \\ 0.80\ CaO\end{matrix}\right\} 0.50\ Al_2O_3 \cdot 4.0\ SiO_2$$

He next determined the most fusible proportion of fluxes keeping the alumina and silica constant. He found that

$$\left.\begin{matrix}0.20 - 0.30\ K_2O \\ 0.80 - 0.70\ CaO\end{matrix}\right\} 0.50\ Al_2O_3 \cdot 4.0\ SiO_2$$

were the most fusible proportions of K_2O and CaO; and of the two, he chose the second and called it cone 4 on account of the amount of silica.

"Graphic Granites as a Source of Feldspar." Watts, *Trans. Amer. Cer. Soc.*, Vol. XV, p. 451, abstracts in part from Vogt.[1] Vogt has offered the theory that, in the graphic granites, the quartz and feldspar are present in eutectic proportions

In this study, Watts indicates that the graphic granites are not deformation eutectics, since they all deform at distinctly higher temperatures than their feldspar components.

Geology of the Pegmatites and Associated Rocks of Maine. Bastin, *Bulletin 445, U. S. Geo. Sur.*, contains a list of analyses including several Maine graphic granites and also foreign specimens. There is considerable variation in the feldspar-quartz ratio, even among those graphic granites whose feldspars are almost identical in composition. In the summary he states: "The theory that the graphic intergrowths in pegmatites represent eutectic mixtures can not be regarded as proved by the published analyses. Certain field evidence is unfavorable to the eutectic theory."

Feldspar and a Deformation Study of Some Feldspar and Feldspar-Quartz Mixtures. Watts, *Trans. Amer. Cer. Soc.*, Vol. XV, p. 144. He found that a mixture of 69 albite and 29 micro-

[1] *Die Silikatschmelz-losungen*, J. H. L. Vogt, 1904, pp. 117-128.

line is the deformation eutectic. This mixture started approximately with cone 6 and was completely deformed, when cone 6 was only half deformed. The albite deformed at about the same rate as the eutectic mixture but proved to be one cone harder. Additions of microline to the eutectic resulted in a decreasing rate of deformation until the potash end of the series was reached, and this had a time-range of deformation equal to twice that of the albite.

Deformation study of potash feldspar-quartz mixtures. The analyses of the feldspar and quartz used are as follows:

	Feldspar	*Quartz*
Ignition loss	0.50	0.11
SiO_2	64.30	99.18
Al_2O_3	19.64	0.00
Fe_2O_3	0.08	0.26
TiO_2	trace	0.01
CaO	trace	0.01
MgO	trace	0.01
BaO	0.17	
K_2O	14.00	99.58
Na_2O	1.32	
	100.01	

It was found that the mixture of 90 percent potash feldspar and 10 percent quartz begins to deform, nearly one-half cone before the pure spar or any other mixture, and completed deformation slightly ahead of the pure spar and at about the same time as the 5 percent quartz admixture. It was shown that a feldspar low in potash and high in soda was very slightly affected by additions of quartz up to 20 percent.

Deformation study of kaolin-feldspar mixtures. Wilson, *Trans. Amer. Cer. Soc.*, Vol. XV, p. 217. This study indicates that there is a deformation eutectic in the region 9-10 percent kaolin and a lesser one in the region 2-3 percent kaolin. In each case, the start is after the pure spar, but the rate is faster, and deformation is completed before the feldspar is deformed. The analysis of the feldspar and also that of the kaolin used is given.

	Feldspar	*Kaolin*
Moisture	0.17	12.22
SiO_2	65.37	46.67
Al_2O_3	17.92	39.02
TiO_2	trace	0.02
Fe_2O_3	0.02	0.11
CaO	0.17	trace
MgO	trace	trace
K_2O	13.05	0.11
Na_2O	2.10	0.25
	98.80	99.45

The ternary system CaO-Al_2O_3-SiO_2. Rankin and Wright, *Am. Jour. Sci.*, p. 25, Jan., 1915. This investigation aimed to treat the system CaO-Al_2O_3-SiO_2 completely and gives the location of eutectics, quintuple points, and boundary curves, together with the corresponding temperatures. Figure 1 shows the location of the different binary and ternary compounds, boundary lines, quintuple points, etc. A quintuple point is the intersection of three boundary lines, and is known as a eutectic, if its temperature is the lowest temperature on the three boundary curves of which it is a common point. In Figure 2, is shown the melting points of the different mixtures with isotherms. It will be noticed that the melting points of all mixtures decrease in the direction of point 2, which is a quintuple point and also a ternary eutectic between pseudo-wollastonite, anorthite and tridymite, melting at 1165+5° C. Altogether eight ternary eutectics and eighteen binary were found. Of these the mixture represented by point 2 has the lowest melting point by 100°C. of any other, the nearest eutectic to it melting at 1265° C.

Other references consulted are listed in the footnote.[1]

[1] Homer F. Staley, Melting Point and Deformation Eutectics, *Trans. Amer. Cer. Soc.*, Vol. VIII.
Day and Allen, Isomorphism and Thermal Properties of the Feldspars, *Am. Jr. Sc.*, Feb., 1905.
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C. N. Fenner, Stability Relations of the Silica Minerals, *Am. Jr. Sc.*, Oct., 1913.

FIG. 1

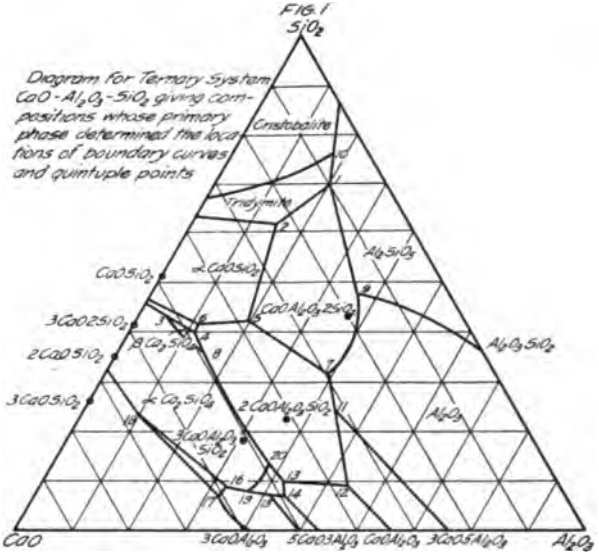
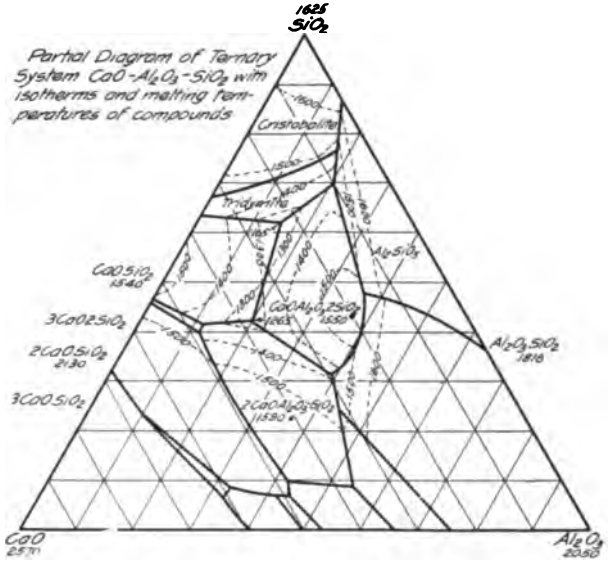

SiO2
Diagram for Ternary System CaO-Al2O3-SiO2 giving compositions whose primary phase determined the locations of boundary curves and quintuple points
Cristobalite
Tridymite
Al2SiO5
CaOSiO2
α CaOSiO2
CaOAl2O3 2SiO2
3CaO2SiO2
β Ca2SiO4
2CaOSiO2
Al2O3SiO2
3CaOSiO2
α Ca2SiO4
2CaOAl2O3SiO2
Al2O3
3CaOAl2O3 SiO2
CaO
3CaOAl2O3
5CaO3Al2O3
CaOAl2O3
3CaO5Al2O3
Al2O3

FIG. 2.


1625
SiO2
Partial Diagram of Ternary System CaO-Al2O3-SiO2 with isotherms and melting temperatures of compounds
Cristobalite
Tridymite
Al2SiO5
CaOSiO2
1540
CaOAl2O3 2SiO2
1550
3CaO2SiO2
2CaOSiO2
2130
Al2O3SiO2
1816
3CaOSiO2
2CaOAl2O3SiO2
1590
CaO
2570
Al2O3
2050

Materials Employed. All oxides were introduced in the form of commercial materials, *i. e.*, feldspar, kaolin and flint. In calculating batches, these were considered as having theoretical composition, and no allowance was made for impurities although an analysis was made for each. The K_2O was introduced as No. 1 Canadian feldspar, the CaO as commercial whiting, the Al_2O_3, not put in as feldspar, was introduced in Florida kaolin, the SiO_2 not contained in the feldspar or kaolin was brought in as Ohio Silica Company's flint.

These were the purest commercial materials obtainable. A chemical analysis was carefully run on each according to the standard methods as in Lord and Demorest's *Metallurgical Analysis*. The analyses are as follows:

	CANADIAN FELDSPAR	FLORIDA KAOLIN	OHIO SILICA FLINT	WHITING
Silica	66.67	45.50	99.40	1.30
Alumina	18.10	39.30	0.20	2.14
Iron oxide	0.10	0.05	0.05	0.10
Lime	0.58	none	none	54.40
Magnesia	none	trace	none	none
Potash	10.915	.42	none	none
Soda	3.74	.44	none	none
Ignition loss	0.20	14.20	0.30	none
Carbon dioxide	.....	.....	.....	42.68
	100.305	99.91	99.95	100.62

Preparation of Materials and Mixtures. The feldspar, quartz and whiting were each passed through a 200 mesh sieve wet. In order to get rid of as much muscovite as possible, the kaolin was passed through a 300 mesh screen. The amount of mica so obtained on the 300 screen was 1.46 percent.

In the preparation of the cones, all material was passed through a 100 mesh screen dry. After weighing a batch, to the nearest hundredth gram, it was placed in a 250 cc. wide-mouth bottle and thoroughly dried at 110° C. The jar was then stoppered, and the batch mixed by agitating vigorously for at least a minute. The dry-mixed batch was then placed in a small

glazed hemispherical porcelain dish. Sufficient water was added to make a smooth paste of such consistency that it was not able to level its own surface and this then was mixed for several minutes with a small pestle. It was thought by this means to obtain the most intimate mixture possible from wet mixing, and owing to the extreme viscosity to prevent precipitation of the

FIG. 3

heavier ingredients. The dish containing the paste was placed in the drying oven and in a few minutes it was dry enough to permit the addition of sufficient dextrine solution to form the cones.

Test Pieces and Test Methods. In order that this study be comparable with those of other investigators, standard size

cones were used as test pieces. All burning was done in a gas-fired, down-draft muffle test kiln especially arranged for this study.

The heat inside the muffle was evenly distributed, as was evidenced by the deformation of the same cone placed in different parts of it. However, in all burns, sufficient standard cones were distributed about the muffle so as to accurately judge of the heat distribution. The rate of heating was indicated by a thermocouple. A rapid increase was maintained to within 200°-250° F. of the initial deformation, and then reduced to 50°-60° F. per hour. The length of burns varied from 24 to 28 hours. The slow rate at the finish was for several reasons, namely:

1. It gave time for a uniform distribution of heat.

2. The cones were evenly heated throughout, and any possible eutectic was given a chance to show signs of activity.

3. The rate of deformation of the cones was slower and more gradual than in quick heating up, and so gave a better chance for accurate observation.

EXPERIMENTAL

Kaolin-Feldspar Study. In this study, it was the purpose to check up results obtained by Wilson (see abstract) and locate any variation due to difference in chemical composition of the materials used. Cones were made of the following mixtures and burned as described previously.

Numbers	1	2	3	4	5	6	7	8	9	10	11
Kaolin	0	2	4	6	8	10	11	12	14	16	20
Feldspar	100	98	96	94	92	90	89	88	86	84	80

Figure 3, upper plaque, shows the result of one burn. The cones from left to right are, standard cones 6, 7, 8; mixtures number 1, 2, 3 , 4, 5, 6, 7, 8.

Results. 1. The pure feldspar starts to deform just after cone 6 and finishes when cone 7 is just starting. 2. Mixtures

containing 6 and 8 percent kaolin start to deform slightly after the pure feldspar but before any other mixture, and also completes deformation slightly after the pure feldspar and before any other mixture. Therefore, this region is considered the deformation eutectic. 3. Since this study aimed to develop the lowest temperature deformation mixture, the composition, 92 percent potash feldspar and 8 percent kaolin was considered the deformation eutectic between these two substances.

Feldspar-Ball Clay Study. It was desired to compare the results of subsituting another clay for the kaolin in the kaolin-feldspar study. Tennessee ball clay was added to the feldspar in the following proportions:

Numbers	A2	A3	A4	A5	A6	A7	A8
Tennessee ball clay	2	4	6	8	10	11	12
Feldspar	98	96	94	92	90	89	88

These mixtures were, in general, about one-eighth cone softer than the kaolin-feldspar mixtures, due in all probability to the higher alkali content of the ball clay. Mixtures A4-5-6-7-8 started to deform approximately with cone 6, but the mixture A5 deformed slightly ahead of cone 6 and before the others. See lower plaque, Fig. 3. It is interesting to note that, although this series is slightly softer than the former, the deformation eutectic in each series contains 92 feldspar-8 clay.

Feldspar-Quartz Study. It was the purpose of this study to check up the results obtained by Watts, (see abstract). Cones were made up and burned as described on pages 13-16. These mixtures had the following compositions:

Number	C1	C2	C3	C4	C5	C6	C9	C7	C8
Quartz	0	2	4	6	8	10	12	15	20
Feldspar	100	98	96	94	92	90	88	85	80

Results. A slight eutectic was apparent with the mixtures 96 percent spar and 4 percent quartz. This cone started to deform after the pure spar, but the rate was faster, and it was slightly ahead at the finish and therefore, is the deformation eutectic. See lower plaque, Fig. 7.

The Most Fusible CaO-Al_2O_3-SiO_2 Mixture. This study was based upon data given by Rankin and Wright (*Amer. Jour.*

FIG. 5

Sc. Jan., 1915). See abstract. Since it is true, that a deformation eutectic is active either coincident with or after a melting point eutectic and for the reason that it melts so far below the others, ternary eutectic No. 2, only, was chosen for study in regard to the deformation eutectic. On page 37, *Am. J. Sc.*, Jan.,

1915, is given the data for the determination of eutectic No. 2 between pseudo-wollastonite, anorthite, and tridymite. This data gives the melting point of the eutectic in these mixtures. The temperature of the quintuple point which is the ternary melting point eutectic in this case, may be determined in any mixture of the solid phases present at that quintuple point, since all mixtures of anorthite, psuedo-wollastonite and tridymite contain more or less of the eutectic composition, and the temperature given is that at which the eutectic melts in a number of compositions.

In order to determine the minimum deformation eutectic of the mixtures given, cones were made up, and the rate and order of deformation noted. The compostitions of the different mixtures and the melting points given are as follows:

Numbers.....	E1	E2	E3	E4	E5	E6	E7	E8
CaO	15	20	25	30	35	15	20	25
Al_2O_3	20	15	10	5	5	25	20	15
SiO_2	65	65	65	65	60	60	60	60
Temp., deg. C..	1172	1175	1175	1165	1170	1166	1171	1172

Numbers.....	E9	E10	E11	E12	E13	E14	E15	E16
CaO	30	25	35	40	20	23.25	15	20
Al_2O_3	10	20	10	5	25	14.75	15	10
SiO_2	60	55	55	55	55	62.00	70	70
Temp., deg. C..	1165	1175	1173	1165	1176	1165	1174	1180

It was found that the melting point eutectic was also the deformation eutectic. This mixture 23.25 CaO, 14.75 Al_2O_3, 62.0 SiO_2 starts to deform just before cone 6 starts and completes deformation when cone 6 is one- third down. The mixture E7 is

half-down when cone 6 has completely deformed. The condition of the rest of the cones is shown in Figure 5.

CaO-Al_2O_3-SiO_2 Eutectic vs. Quartz Mixtures. The eutectic just determined expressed in empirical, molecular formula is:

$$1.00\ CaO\ .\ 0.348\ Al_2O_3\ .\ 2.489\ SiO_2$$

The object of this series was to find out whether or not the addition of quartz or the substraction of quartz from this formula would lower the deformation point . This was made the middle of the series, quartz being added or substracted at the rate of one-tenth equivalent. The mixtures were made up as follows:

Number	CaO	Al_2O_3	SiO_2
D0	1.00	.348	1.5
D1	1.00	.348	2.0
D2	1.00	.348	2.1
D3	1.00	.348	2.2
D4	1.00	.348	2.3
D5	1.00	.348	2.489
D6	1.00	.348	2.6
D7	1.00	.348	2.7
D8	1.00	.348	2.8
D9	1.00	.348	2.9
D10	1.00	.348	3.0
D11	1.00	.348	3.5

Here as in the previous study, it was found that the melting point eutectic is the deformation point eutectic. Additions and subtractions of silica alike hardened the eutectic mixture. Mixtures D4 and D6 next to the eutectic, followed immediately after but other mixtures had not commenced to deform with cone 6 half-down, although there was evidence of fusion in several. Upper plaque Fig. 5.

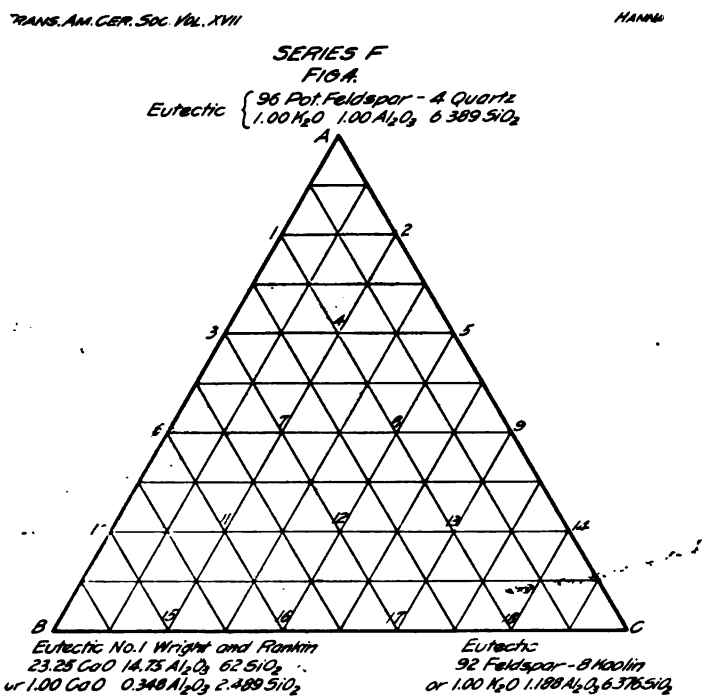
Blending of the Most Fusible Mixtures of K_2O-Al_2O_3-SiO_2 vs. CaO-Al_2O_3-SiO_2. The following eutectics, which have been developed by this study, were made the end members of a triaxial. See Figures 4 and 6.

A. 96 Pot. Feldspar 4 Quartz

B. 23.25 CaO 14.75 Al_2O_3 62.0SiO_2

C. 92 Pot. Feldspar 8 Kaolin

End members were mixed dry by screening several times and also by drying them out thoroughly and agitating vigorously in a closed jar. End members were blended on a percentage-by-weight basis, but all intermediate members were blended on



a molecular basis. Cones were made and burned in the usual manner as described.

Blend F3 is the first to start, deforming at the same time as standard cone 3, but the rate is faster, and it is completely deformed when cone 3 is only three-fourths deformed. Blend F7 is the next and is one-half down when cone 3 is completely deformed.

Blend F12 is the next to start deforming and is one-fourth down when cone 3 is completely deformed. The formulae of these are:

Blend F3 $\left.\begin{matrix}0.6\ K_2O \\ 0.4\ CaO\end{matrix}\right\}$ $0.739\ Al_2O_3$ $\left\{\right.$ $4.829\ SiO_2$

FIG. 6

Blend F7 $\left.\begin{matrix}0.6\ K_2O \\ 0.4\ CaO\end{matrix}\right\}$ $0.777\ Al_2O_3$ $\left\{\right.$ $4.830\ SiO_2$

Blend F12 $\left.\begin{matrix}0.6\ K_2O \\ 0.4\ CaO\end{matrix}\right\}$ $0.8144\ Al_2O_3$ $\left\{\right.$ $4.824\ SiO_2$

By reference to the triaxial, Fig. 4, it will be seen that the amount of the eutectic, $CaO\ Al_2O_3\ SiO_2$ is constant in the first three cones to deform and that the only difference in the composition of F3-7-12 is the substitution of the potash feldspar kaolin eutectic for the potash feldspar—quartz eutectic, which in reality only changes the amount of Al_2O_3 in the molecular formula increasing it, the R O and SiO_2 remaining constant. This is apparently a beautiful illustration of the fact that an excess of alumina results in a pronounced increase in viscosity.

The general results of this series is the temperature reduction of 1¼ cone, below the most fusible mixture established by Dr. Seger, who found that the most fusible mixture was cone 4, *i. e.:*

$$\left.\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}\ 0.5\ Al_2O_3\ \left\{\ 4.SiO_2\right.$$

Study of the Most Fusible Mixture of Eutectic 69 Albite, 29 Microcline and the Eutectic 23.25 CaO, 14.75 Al_2O_3, 62 SiO_2. The purpose of this study was to ascertain whether or not the deformation temperature obtained in the foregoing study could be lowered by the introduction of soda. This was introduced in the form of soda feldspar mixed in the eutectic proportion with potash feldspar (see abstract). This mixture was blended with the CaO-Al_2O_3-SiO_2 eutectic to form a series of six numbers.

The analysis of the albite used is as follows:

	percent
H_2O	0.20
SiO_2	68.18
Al_2O_3	20.12
Fe_2O_3	0.05
TiO_2	trace
CaO	0.85
MgO	0.05
K_2O	0.66
Na_2O	9.38
	99.49

The albite and the microcline used in this and the previous study have the following calculated mineral analysis:

	ALBITE	MICROCLINE
Soda feldspar	79.124	31.597
Potash feldspar	3.892	64.108
Clay	8.658	.256
Quartz	6.60	3.816
Other impurities	1.15	.60
	99.424	100.377

The empirical molecular formulae of the two end members are:

$$\text{G-D:}\quad \left.\begin{matrix}0.7157\ Na_2O\\ 0.2829\ K_2O\end{matrix}\right\} 1.151\ Al_2O_3 \left\{ 6.858\ SiO_2$$

$$\text{G-E:}\quad 1.00\ CaO \quad 0.348\ Al_2O_3 \quad 2.489\ SiO_2$$

Mixture G-1 starts to deform when cone 2 is only one-half down. Mixture G-3 starts when cone 2 is just about down, but the rate of deformation is much faster than G-1, and it is completely deformed about one-fourth cone ahead of G-1 and when standard cone 3 has just started. See upper plaque, Fig. 7. The empirical molecular formula of these two mixtures are:

$$\text{G-1}\quad \left.\begin{matrix}0.549\ Na_2O\\ 0.217\ K_2O\\ 0.256\ CaO\end{matrix}\right\} 0.973\ Al_2O_3 \left\{ 5.904\ SiO_2$$

$$\text{G-3}\quad \left.\begin{matrix}0.358\ Na_2O\\ 0.142\ K_2O\\ 0.500\ CaO\end{matrix}\right\} 0.748\ Al_2O_3 \left\{ 4.71\ Sio_2$$

It is shown by this study, that by the use of the potash-soda feldspar eutectic the deformation temperature of the previous series was reduced almost one cone and that of Dr. Seger almost two cones.

This study does not, however, apply to the solution of the problem as undertaken, since Na_2O is here employed.

General Conclusions. As a result of this study, the mixture of K_2O-CaO-Al_2O_3-SiO_2 with lowest fusing point has been

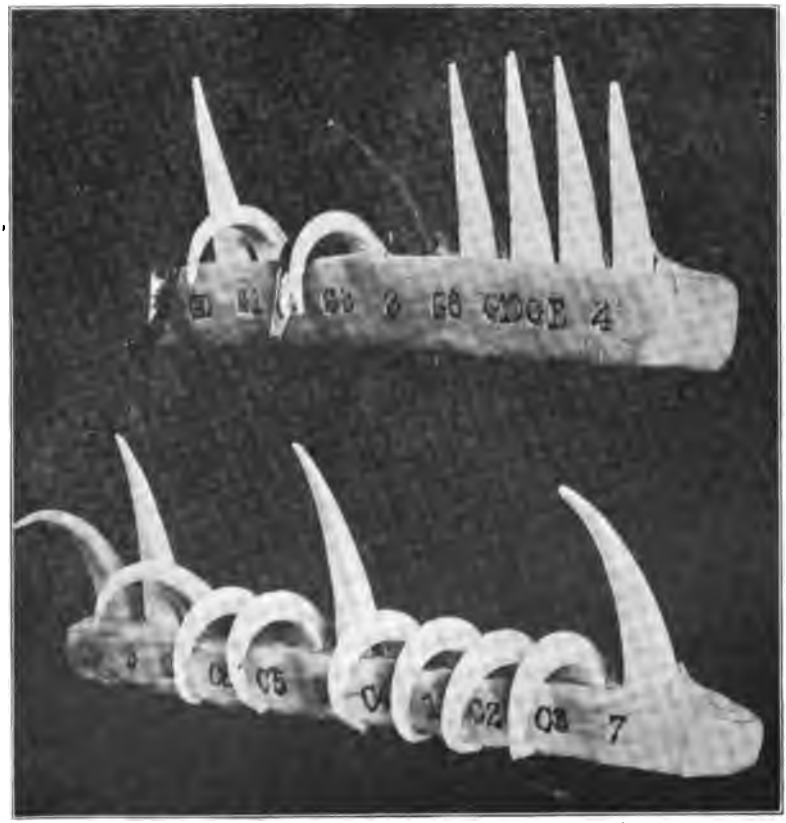


FIG. 7

determined. It starts to deform with standard cone 3 but is completely deformed when cone 3 is only three-fourths deformed. Its composition is:

$$\left.\begin{matrix} 0.60\ K_2O \\ 0.40\ CaO \end{matrix}\right\}\ 0.739\ Al_2O_3\ \left\{\ 4.829\ SiO_2\right.$$

CHEMICAL CONSTITUTION	MINERAL ANALYSIS	NORM. CONSTITUTION
65.27 SiO_2	333.6 Feldspar	4.32 Feldspar
16.98 Al_2O_3	40.0 Calc. carb.	1.00 Anorthite
5.04 CaO	35.86 Kaolin	1.87 Wollastonite
12.71 K_2O	57.06 Quartz	4.96 Quartz
100.00	466.52	

The natural continuation of this investigation is a study of the influence of the $ZnO.Al_2O_3.SiO_2$ eutectic (if one exists) or $ZnO\ SiO_2$ eutectic upon the most fusible mixture found in this investigation.

FACTORY PRACTICE IN THE CASTING OF CLAY WARE.[1]

DISCUSSION

Mr. Bleininger: I would like to ask Mr. McDougal what effect he has found with regard to the length of time the slip remains in the tank? I ask this question because no particular pains are apparently taken in this connection; sometimes we work with three and sometimes five day slips, and I know that on several occasions the slip became "livery." I would like to hear Mr. McDougal's opinion about this point. It is quite evident, that it is a very serious difficulty, and it ought to be realized that, if casting is to be done, we should adopt some kind of a standard in regard to the length of time the slip is to stand. Of course, you can lengthen the time by appropriate additions of reagents, but the fact should be taken into account. Likewise, it has been found, that temperature is quite an influential factor; it makes a great deal of difference in regard to the behavior of a slip whether the temperature is 60 or 70 degrees F. or higher. One more point—having become curious in regard to the effect of gases and air in the slip, we subjected in a number of cases, slip to a vacuum treatment, and we found that the viscosity of the slip was increased very markedly, and the amount of air we got out of the slip was very surprising. In order to find whether or not any decrease in the volume of the slip had taken place, we used the burette but were not able to detect any decrease in volume due to the removal of this air by the vacuum. Just how that air is held in the slip is not quite clear. It is evidently absorbed in the very structure of the clay and some of it, of course, is dissolved in water.

Mr. McDougal: As to the question of time, the first 24 hours is a very important period during which changes do occur which might affect the character of the slip. This is lessened, however, if the slip is thoroughly blunged, beat up, not merely stirred, when the salts are added. If the slip is merely stirred,

[1] Discussion following an informal talk by Mr. Taine G. McDougal. The subject matter of the talk to be published in detail by the U. S. Bureau of Mines.

and run into the reserve cistern, where it is agitated merely enough to prevent settling, variations will continue to occur until that slip is made homogenous, but, if it is thoroughly blunged in the first place, after the first 24 hours, there should be no variations which would give complications in the result. As to temperature—the temperature in a commercial slip room at one time during the winter, went down to four degrees centigrade, that's four degrees above freezing. Of course we found it was impossible to cast the slip at this temperature. The same slip at normal temperature, say 30 degrees C., was cast very successfully, so it is very evident that the temperature has a marked influence on the casting behavior of the slip, a reduction of temperature having an effect analagous to a reduction in the salt concentration, an increase having an effect analagous to an increase in the salt concentration.

Mr. Purdy: Mr. McDougal spoke about the concentration of salt which would be best for casting. I wish to inquire what percentage of salt you would use for good castings? Where would you choose it from the curve?

Mr. McDougal: With a given clay or body, that depends entirely upon the thickness of the piece you want to cast; the thicker the piece you have to cast, the more open the body has to be to get that thickness cast, and the more open the body has to be, the greater the concentration of salt required.

Mr. Purdy: As an illustration, of how to read the curve, Fig. 1, let me ask if you cast here, (indicating the lowest points on the curve), would you have your bodies stick tight to the mold?

Mr. McDougal: Yes, sir.

Mr. Purdy: And if you should cast with the concentration past the min. point they would come away from the mold easily?

Mr. McDougal: I have never experimented with large batches on that side of the curve.

Mr. Purdy: Then if you wanted the cast to come away from the mold easily—?

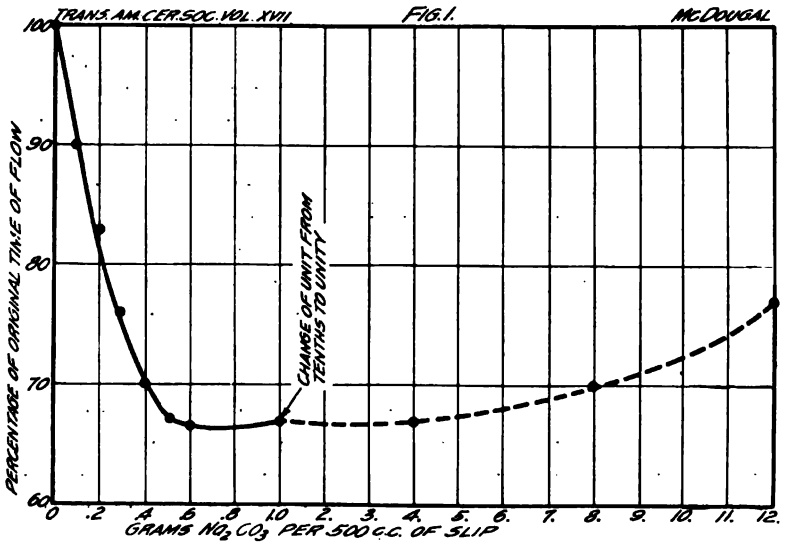
Mr. McDougal: I would start at the top (left) and come down feeling for the least amount which would serve the purpose.

At the lowest point, you would be depending for the strength of your body entirely upon the sodium silicate which might be added, which material has a mechanical stickiness which might be relied upon to partly replace the strength lost, as the salts convert the gel of the clays to the sol state.

Mr. Swalm: Does that mean that the thicker the piece the more the salt needed?

Mr. McDougal: It does.

Mr. Purdy: The thickness that you referred to was the density of the slip?



Mr. McDougal: No, the thickness of the cast.

Mr. Purdy: About what percentages would you use in a body?

Mr. McDougal: It depends entirely upon the quantity and quality of the clays present, but to give you a general idea, I would say from two-tenths to five-tenths of one percent each, sodium carbonate and sodium silicate, the sodium silicate being 40° Beaume scale, and the carbonate, the commercial crystalline sodium carbonate.

Mr. Weelans: Do you mean a saturated solution of your carbonate?

Mr. McDougal: It would be added to the blunger after having been dissolved in water but would be weighed as crystalline commercial sodium carbonate.

Mr. Purdy: In regard to the mixture of salts used in the casting; is it best to use straight soda ash or straight silicate of soda, or a mixture of the two?

Mr. McDougal: That is a hard question to answer satisfactorily. Of course the requirements of a slip are more exacting, as you get into the heavier ware. Now with light dishware, as hotel china, you could probably get satisfactory slips by the use of sodium carbonate alone, or sodium silicate alone, but when you come to the heavier ware, you have to approximate the maximum effect and get down to the minimum point on the curve you have been referring to, and approximating that point sodium silicate must be introduced to give bonding strength to the piece of ware. You cannot use sodium silicate alone in some cases, because sodium silicate is itself a sticky gel colloid and would interfere with the casting of the ware just the same as the clay gel does which you are trying to get rid of.

Mr. Weelans: Was it double casting or pouring off that you were speaking of? There are two different kinds of castings.

Mr. McDougal: My experience was with cases which required both, the single casting and the double casting together with a third classification called over-casting, where a piece is cast one day, allowed to stiffen over night to not quite leather hardness and then incorporated into the final piece of ware on the second day.

Mr. Weelans: You also spoke of an open body when you were speaking about Fig. 1. What did you mean by that?

Mr. McDougal: One which will allow water to continue to pass through the layer which adheres to the mold, until the desired thickness of ware has been obtained.

Mr. Weelans: What facilitates that condition?

Mr. McDougal: The conversion of the gel in the clay to the sol.

Prof. Parmelee: You speak of two-tenths and five-tenths percent, is that two-tenths and five-tenths percent. of the weight of the dry body?

Mr. McDougal: Yes, although salt additions should be better based on the volume of the slip.

Prof. Stull: One of the greatest troubles in controlling the casting slip containing electrolytes is due to the slow velocity of reaction towards equilibrium. If you measure the viscosity of a slip you get a certain value; measure it an hour later, and you get a different value, and if the viscosity is measured a day later, a third value is obtained. In fitting a slip to a plastic fire-clay body, about the minimum amount of clay allowable in the slip is 45 percent; if you get much below that amount, flaking begins to appear unless glue or some other substance is introduced to make it adhere. One of the problems which is desirable of solution in the enamel brick business is to develop an enamel which can be applied directly to a plastic fire-clay body, not a leather hard body, but one as plastic as the clay is when it issues from the die. The maximum amount of clay that can be put into an enamel (and have a glossy enamel) is about 30 percent. Enamels, when applied to a stiff-mud body, flake in drying due to their low clay content and therefore low shrinkage and poor adhesion. Here is a problem opposite to the casting slip problem in that it is desirable to coagulate instead of deflocculate, and thereby increase the shrinkage and, if possible, the adhesion of the enamel. By using the Mariotte tube for measuring the viscosity of enamels containing variable amounts of coagulants, we get very abrupt max points which show very sensitive changes with respect to time. Sometimes the enamel will thicken, so that it will not flow, then a little later become very fluid. Here is a problem difficult to solve, because these enamels contain a comparatively high percent of calcium carbonate, and the ordinary acids cannot be used as coagulators on this account. We are practically limited to a few divalent, trivalent and quadrivalent salts as coagulants. The most promising results seem to be obtained by silicic acid formed in the enamel by sodium silicate and oxalic acid. In this case, abrupt max points also occur which fluctuate on account of the instability and the time factor. If

the enamel is applied when it has attained the proper consistency, a perfect fit results, but if applied a few hours earlier or a few hours later, either cracking or flaking occurs. In the casting process, it is more than likely that some of the difficulties encountered are due to the slow physical, and to a degree, chemical action going on in the colloidal matter of the slips.

Mr. Purdy: May I ask if there is any difference in effect given by the rate at which you run your blunger, when you are adding your salts?

Mr. McDougal: Yes, I think that I brought that out when I said the slip would not vary after the first 24 hours, if it had been thoroughly beaten up when the salts were added. If the salts are not thoroughly mixed in at the start, and it takes thorough blunging to do that, you will get into trouble.

Mr. Bleininger: We found that this change in consistency is more likely to take place when you work to the left of viscosity minimum; with a larger amount of reagents, the difficulty is diminished.

Mr. McDougal: You mean that as the slip becomes thinner through the use of a larger amount of reagents?

Mr. Bleininger: Yes.

Mr. McDougal: That makes the mixing more easy to accomplish.

THE EFFECT OF SALTS ON THE DRYING BEHAVIOR OF SOME CLAYS

BY HOMER F. STALEY, IOWA STATE COLLEGE

Several articles have been published during the last few years dealing with the effect of salts on the volume shrinkage during drying of clays made up in the plastic state. Among these may be mentioned the publications by Bleininger,[1] Bleininger and Fulton,[2] Kerr and Fulton,[3] and Back.[4] Incidental to their treatment of other problems, several investigators have noted[5] that the addition of common salt, NaCl, reduced the cracking of certain clays during drying. In fact, the use of salt for this purpose is not at all new. One manufacturer, at least, in Iowa has been employing it for many years with excellent results. Inasmuch as many clays in Iowa are difficult to dry, and the data cited show that small amounts of salts have a decided effect on the drying behavior, it seemed desirable to make a study of the subject in relation to Iowa clays.

While the work that had been done on volume shrinkage was of considerable interest, the results obtained did not seem to account for the remarkable effect of salts in reducing cracking. It was, therefore, decided to attack the problem mainly from the standpoint of the effect of salts on the rate of drying. Arrangements were also made for determining linear shrinkage, the amount of cracking and the stage of the drying at which it occurs.

EXPERIMENTAL WORK

Procedure. In making up a series of samples, the salts were dissolved in or mixed into the tempering water. The clays were then thoroughly tempered by hand and made into half bricks 4½ in. by 4½ in. by 2¼ in. in size. This size gives a dry-

[1] *Orig. Com. 8th Intern. Congress Appl. Chem.*, V, 17-32.
[2] *Trans. Amer. Cer. Soc.*, XIV, 827, 839.
[3] *Trans. Amer. Cer. Soc.*, XV, 184-192.
[4] *Trans. Amer. Cer. Soc.*, XVI, 515-546.
[5] Keele, *Trans. Amer. Cer. Soc.*, XIV, 154.
Bleininger, *Orig. Com. 8th Intern. Congress Appl. Chem.*, V, 24.
Rainey, *Trans. Amer. Cer. Soc.*, XVI, 406.

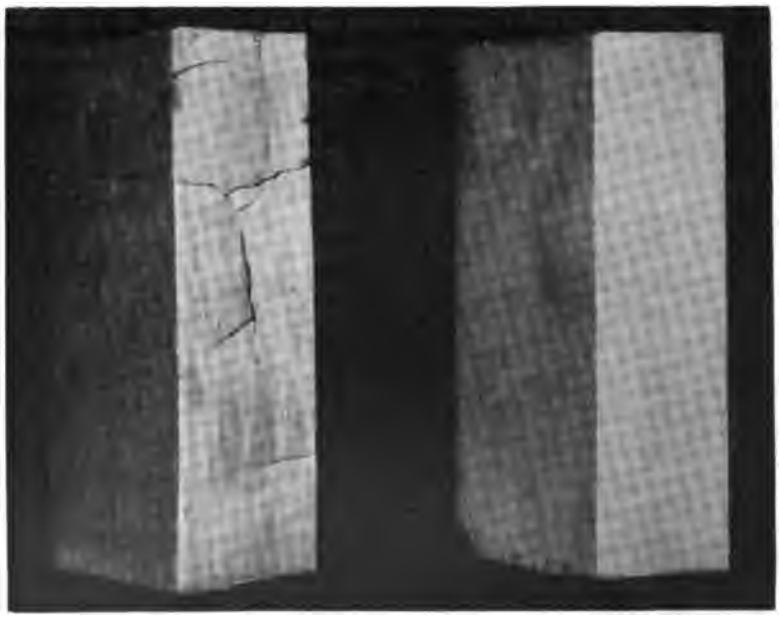
ing effect similar to that of whole bricks. The first samples made in a series were put into a wet closet until the last ones were finished, and the completed series was kept in the closet for several hours. The whole series was then allowed to start drying under predetermined conditions. While these conditions, no doubt, varied somewhat during the drying period, all the samples in a series were exposed equally to the effect of the variation. The results for any one series, therefore, show the effect of various amounts of different salts on samples of clay made up and dried under the same conditions.

The points noted in drying behavior were: rate of loss of water, amount of cracking, and, as far as possible, linear shrinkage. No attempt was made to determine volume shrinkage, first, because it was feared that the immersion of the wet samples in oil, which is necessary in volume shrinkage determinations, would have some effect on drying behavior, and second, because such measurements cannot be made on clays that crack badly in drying. In fact, on account of the prevalence of cracking in our samples and the inherent crudeness of linear shrinkage methods, we do not claim a high degree of accuracy for the individual shrinkage measurements.

Iowa Loess Clay. In the northern part of the Mississippi Valley, west of that river, occur vast areas of loess clays. Two-thirds of the state of Iowa is covered with these clays. They are supposed to be wind blown deposits. They are really mixtures of limey red-burning clay with large proportions of fine grained sand. The leanest ones are clayey sands, similar to molding sand, and those richest in clay would be classified as very sandy clays.

In many localities, these loess clays are the only ones available even for the manufacture of common brick and drain tile. Owing to the large amount of sand they contain, they are not plastic enough to make large size tile, but for the manufacture of common brick and small drain tile, they have several advantages. They are soft and unconsolidated. Therefore, they are easy to dig and require no grinding. As a rule, they vitrify gradually and are therefore easily handled in burning. For-

merly, these clays were worked in hundreds of small yards, but these plants are rapidly ceasing to operate on account of the great difficulty of drying the clays without cracking. The less sandy clays work the best both in manufacture and drying. Since the tenderness of the clays is due to lack of sufficient plastic bonding material, preheating treatment simply aggravates the trouble. Any economical method of rendering these clays safer to dry is a decided advantage.



Illustrating the effect of common salt in reducing cracking during drying of a loess clay. The only difference in composition and manufacture was that the brick on the right contained an addition of ½ of 1 percent of common salt.

In Table I are shown the data for the effect of sodium chloride (common salt) on the drying behavior of a typical loess clay. The rate of drying is shown graphically in Figure 1. It will be noted that the addition of salt decreased the rate or drying, increased the amount of hygroscopic water in the clay increased the shrinkage, and decreased the cracking. We have obtained similar results with several loess clays dried under various con-

ditions. In all cases, the cracks appear during the first four or five hours of drying, grew wider for a time, but about the time shrinkage ceased tended to close up.

In Table II, are shown the data for the effect of sodium carbonate (soda ash) on the same clay. Figure 2 shows the rate of drying in curve form. These samples were made up and dried along with those containing sodium chloride. The first small addition of sodium carbonate increased the rate of drying at all times, but larger additions decreased it slightly during the bulk of the drying period and increased it very slightly at the end. Sodium carbonate decreased hygroscopic water, reduced shrinkage and increased cracking. The cracks all appeared in the first few hours of the drying.

Dakota Joint Clay. In many parts of the northern Mississippi Valley, so-called "joint" clays are found. These are sticky plastic clays that warp badly in drying and tend to crack into cube-like forms. These clays are found in several parts of Iowa, but one from South Dakota was chosen for experiment because it had failed to respond to preheating, the usual method of treatment.

In Table III and Figure 3, are shown the effects of sodium chloride on this joint clay. The results are similar to those obtained with loess, the only difference being that little effect on shrinkage was noticeable. In Table IV and Figure 4 are shown data for sodium carbonate. In this case, the first small addition of the salt increased the drying rate throughout, and larger additions decreased it. Small additions decreased hygroscopic water, but larger ones increased it. Sodium carbonate had small effect on shrinkage, but had a strong tendency to produce cracks. These all appeared during the first few hours of the drying.

Woodward Shale. The effects of the soluble salts commonly found in clays have considerable interest. In connection with some other work, we found it necessary to add calcium and magnesium sulphates to a red burning shale from near Woodward, Iowa. In Table V and Figure 5, are shown the results for magnesium sulphate. It will be noted that magnesium sulphate decreased the rate of drying and increased the amount of hygro-

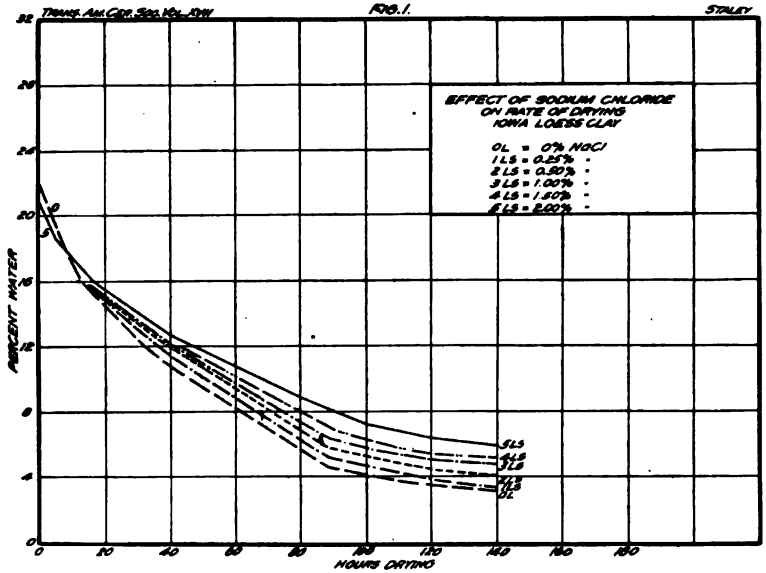

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FIG. 1.
STALEY
EFFECT OF SODIUM CHLORIDE ON RATE OF DRYING IOWA LOESS CLAY
0L = 0% NaCl
1LS = 0.25% "
2LS = 0.50% "
3LS = 1.00% "
4LS = 1.50% "
5LS = 2.00% "
PERCENT WATER
HOURS DRYING

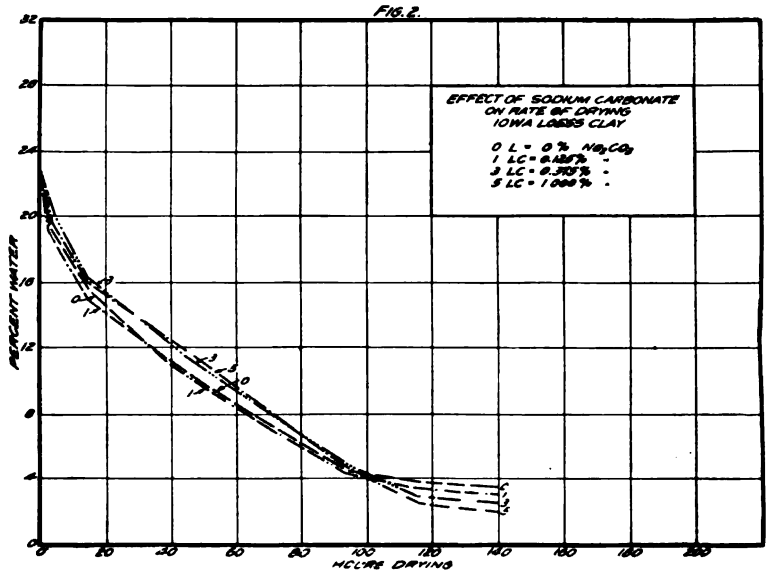


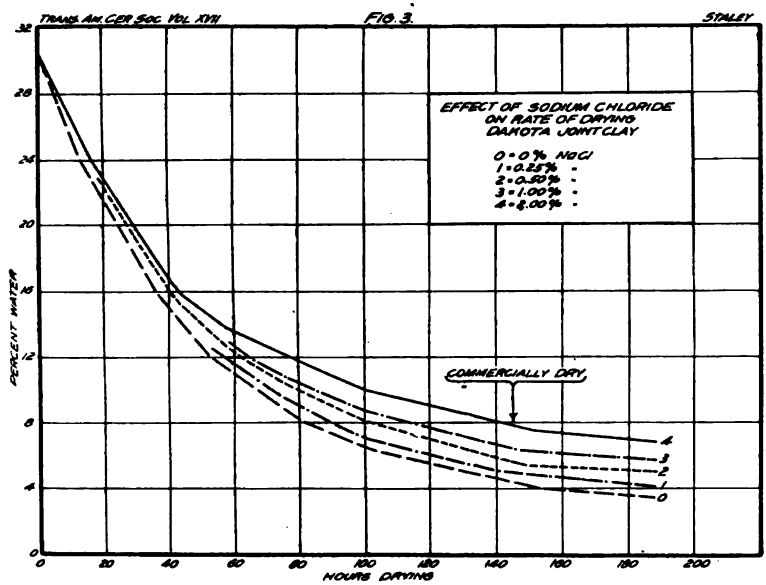
FIG. 2.
EFFECT OF SODIUM CARBONATE ON RATE OF DRYING IOWA LOESS CLAY
0 L = 0 % Na2CO3
1 LC = 0.167% "
3 LC = 0.750% "
5 LC = 1.000% "
PERCENT WATER
HOURS DRYING

scopic water. There was no noticeable effect on shrinkage and no cracking in any of the samples. Unfortunately, this clay proved to be naturally safe drying, and so not well adapted to demontrating the effect of the salts on cracking. However, we found in another series of experiments that magnesium sulphate did decrease cracking of tender clays.

In Table VI and Figure 6, are shown the results for calcium sulphate with the same clay. The first addition reduced the rate of drying at all stages. Larger additions increased the rate of drying very decidedly in the early stages and decreased it slightly at late stages. The calcium sulphate increased hygroscopic water. The shrinkage was reduced, and no cracking occurred. It is believed that the chemical action of calcium sulphate is similar to that of magnesium sulphate and is really exemplified by the effect of the first small additions. The peculiar effect of larger additions of calcium sulphate in hastening the drying is thought to be due to the crystallization of the bulk of the calcium sulphate as soon as the water began to be evaporated from the clay. It will be remembered that calcium sulphate is sparingly soluble. The growth of calcium sulphate crystals would tend to open up the clay and allow drying to take place more rapidly.

Effect on Color. While both common salt and soda ash increased the amount of scum formed in drying, they caused no scum on the burned ware. In fact, in one case a clay, that showed considerable scum on the burned trials when no salts were used, showed progressively decreasing amount of scum on the burned ware as the amount of either sodium chloride or soda ash was increased. Evidently, the heavy scums formed by sodium chloride and soda ash in drying had served to volatilize or flux into the body the normal non-volatile and infusible scum. In general, the only effect of soda ash was a slight darkening of the color of the ware. On the other hand, sodium chloride produced clearer and brighter colors. This is no doubt due to volatilization of iron chloride.

Rather to our surprise, additions of calcium sulphate in amounts up to 3 percent. to a clay free from soluble salts did not cause scumming. This is probably due to the comparatively


TRANS. AM. CER. SOC. VOL. XVII
FIG. 3.
STALEY
EFFECT OF SODIUM CHLORIDE ON RATE OF DRYING DAKOTA JOINT CLAY
0 = 0 % NaCl
1 = 0.23 % -
2 = 0.52 % -
3 = 1.00 % -
4 = 2.00 % -
COMMERCIALLY DRY
PERCENT WATER
HOURS DRYING
0
4
8
12
16
20
24
28
32
0
20
40
60
80
100
120
140
160
180
200
0
1
2
3
4

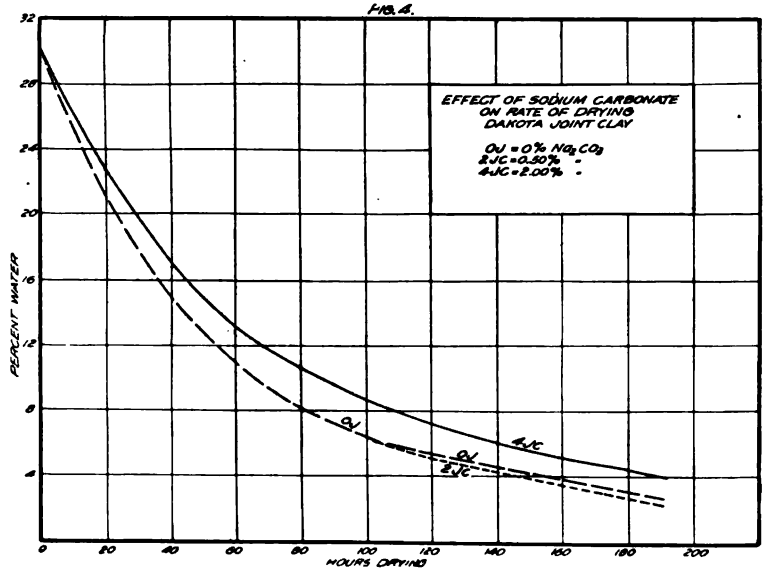


FIG. 4.
EFFECT OF SODIUM CARBONATE ON RATE OF DRYING DAKOTA JOINT CLAY
0J = 0 % Na2CO3
2JC = 0.30 % -
4JC = 2.00 % -
PERCENT WATER
HOURS DRYING
0J
2JC
4JC
4
8
12
16
20
24
28
32
0
20
40
60
80
100
120
140
160
180
200

small solubility of calcium sulphate in water (approximately 1 part in 500 of water) and the marked hastening of the drying caused by this salt. Magnesium sulphate and mixtures of magnesium sulphate with calcium sulphate produced copious scumming.

Effect on Vitrification. The effect of salt additions on vitrification was appreciable in the cases of sodium carbonate and sodium chloride. The first was to be expected; but owing to its volatile nature, the fluxing action of a small amount of salt was a matter of conjecture. We had an opportunity to determine the fluxing effect of a small addition of salt in three clays. The effects on absorption are shown in Table VII and Figure 7, and those for fire shrinkage are shown in Table VIII and Figure 8. Clay A was a typical loess clay. Clay B was made up of a mixture of 80 percent. of Clay A and 20 percent. of a fine grained shale. Clay C contained 60 percent. of Clay A and 40 percent. of the shale.

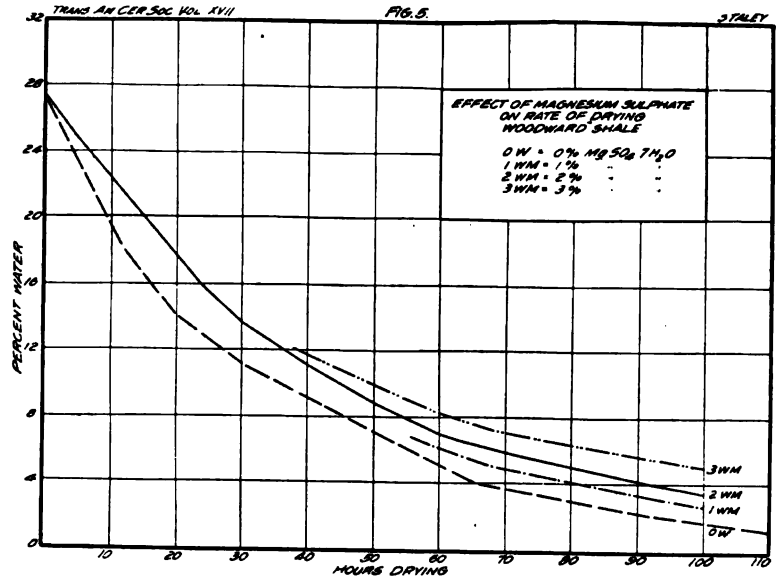
From a study of the data, it is seen that the addition of one-half of one percent of common salt had the following rather remarkable combination of effects.

1. It reduced the heat treatment necessary to produce a given degree of vitrification by from one to three cones.

2. It enabled a more nearly complete degree of vitrification to be produced than was at all possible in the case of the untreated clay.

3. The temperature of overfire was not lowered. This, in connection with the effects noted in 1 and 2, produced a much longer and safer vitrification range.

As might be expected from the vitrification behavior of sandy clays, the most marked and beneficial effect of salt on vitrification was produced in the loess. As the mixtures became less sandy, the effect of the salt was less noticeable. As the result of these experiments, one-half of one percent of common salt is now being used with Clay A in the manufacture of brick in an Iowa factory. The results are even better than were hoped for from the laboratory tests. Cracking in drying is reduced. The firing temperature is lowered to such a degree that the saving of fuel


TRANS AM CER SOC VOL XVII
FIG. 5.
STALEY
EFFECT OF MAGNESIUM SULPHATE ON RATE OF DRYING WOODWARD SHALE
0 W = 0% Mg SO4 7H2O
1 WM = 1% " "
2 WM = 2% " "
3 WM = 3% " "
PERCENT WATER
HOURS DRYING
3WM
2 WM
1 WM
0W

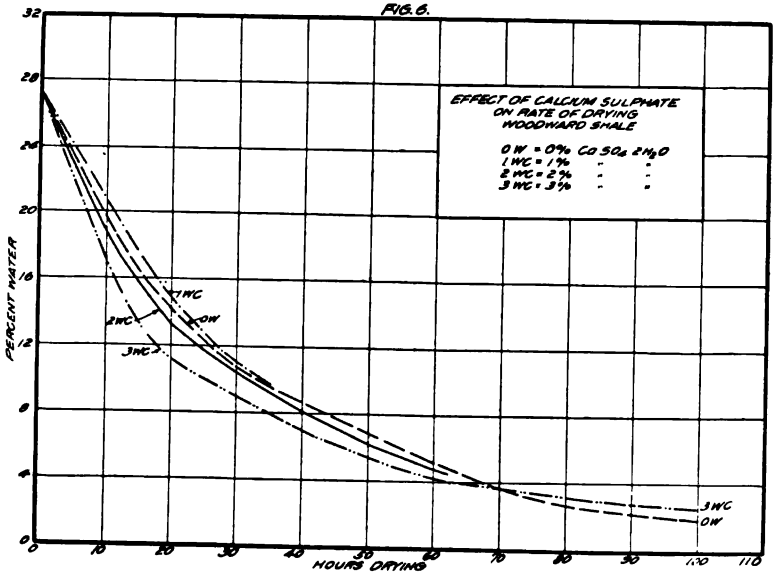


FIG. 6.
EFFECT OF CALCIUM SULPHATE ON RATE OF DRYING WOODWARD SHALE
0 W = 0% Ca SO4 2H2O
1 WC = 1% " "
2 WC = 2% " "
3 WC = 3% " "
PERCENT WATER
HOURS DRYING
1WC
2WC
3WC
0W

more than pays for the salt treatment; and the product is absolutely free from scum.

Theoretical Explanation. It is not feasible to give in this paper a detailed discussion of the many interesting theoretical considerations involved in the effect of salts on the drying behavior of clays We can only mention a few points.

A. Any salt dissolved in water lowers the vapor pressure of water and its rate of evaporation. Other things being equal, it will also increase the amount of hygroscopic moisture on any surface.

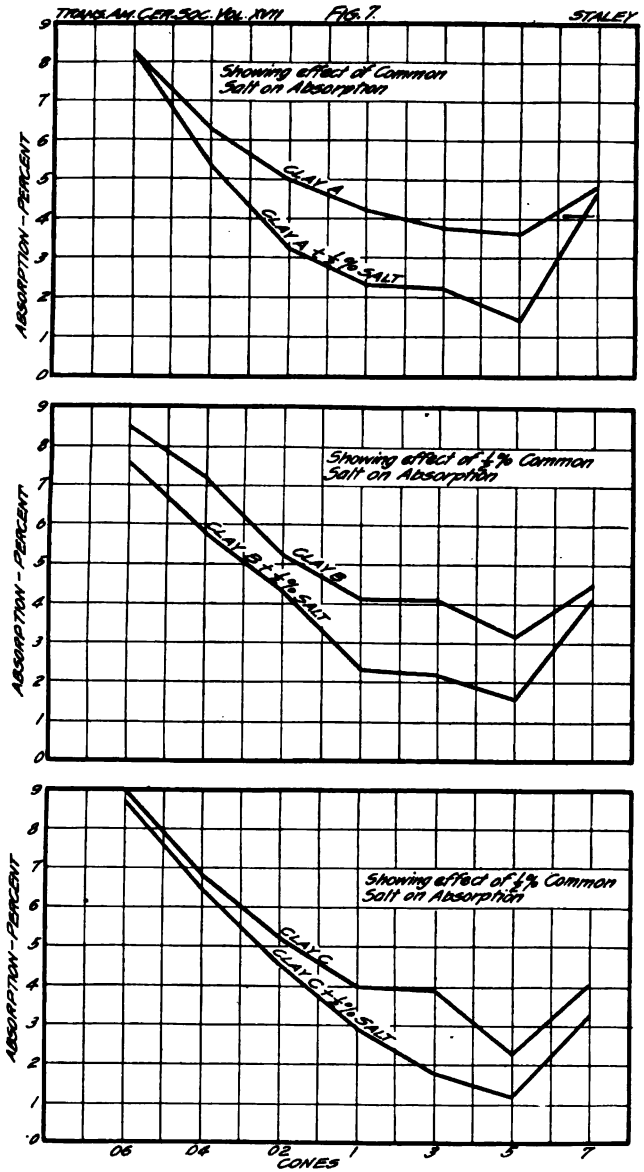
B. Salts that cause deflocculation of the particles of clay of colloidal (very minute) size tend to produce an open structure in the clay that favors rapid evaporation and poor capillary action.

C. Salts that cause flocculation tend to produce a structure permeated by a multitude of fine capillary channels. This produces slow evaporation from the surface of the ware and adequate replacement of the evaporated water by a supply drawn from the interior of the ware by capillary action.

From the data presented, it will be seen that, in nearly every case, whatever cracking occurred took place in the early stages of drying, when there was little difference in the amount of drying that had taken place or in the rate at which it was progressing at the time. The difference was that, in the case of the untreated clays and the clays treated with deflocculants, (for these particular clays in the proportions used), the drying took place largely from the surface layers. In the case of clays treated with coagulants as fast as moisture was evaporated from the surface, it was replaced by water drawn from the interior of the sample by capillary action.

CONCLUSIONS

Soda ash, *i.e.*, anhydrous sodium carbonate (Na_2CO_3), decreased the rate of drying as a whole in the clays studied and increased the tendency to cracking. It had a tendency to lengthen the vitrification range, but would not be an economical or de-


TRANS. AM. CER. SOC. VOL. XVII FIG. 7 STALEY
Showing effect of Common Salt on Absorption
CLAY A
CLAY A + 1% SALT
ABSORPTION - PERCENT
Showing effect of 1% Common Salt on Absorption
CLAY B
CLAY B + 1% SALT
ABSORPTION - PERCENT
Showing effect of 1% Common Salt on Absorption
CLAY C
CLAY C + 1% SALT
ABSORPTION - PERCENT
06 04 02 CONES 1 3 5 7

sirable addition to most clays for ordinary processes of manufacture.

Common salt (sodium chloride—NaCl) decreases the rate of drying at all times, in most cases increases shrinkage, produces better colored ware, and has a beneficial effect on vitrification behaviors especially in sandy or loess-like clays. The use of additions of common salt in amounts of from one-fourth percent to possibly two percent of the weight of the clay is a feasible method of rendering workable many of the clays of Iowa that give trouble in drying and burning.

The use of magnesium or calcium sulphate as an addition to clays would not be desirable on account of the harmful effect on the burning properties of the clay.

The reduction of cracking in drying is due to the fact that certain salts (coagulants under the given conditions) produce a structure favorable to capillary action, and therefore as fast as moisture is evaporated from the surface of the ware, it is replaced by water from the interior.

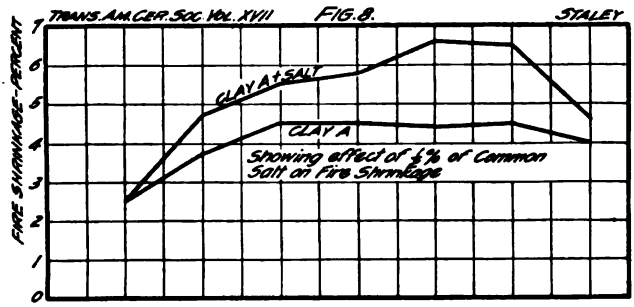
DISCUSSION

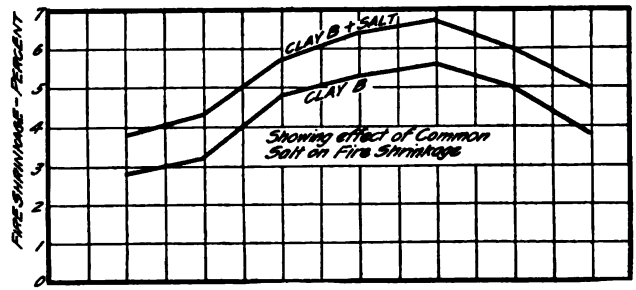
Mr. Ogden: In most of these case, was the cracking reduced by the addition of these salts?

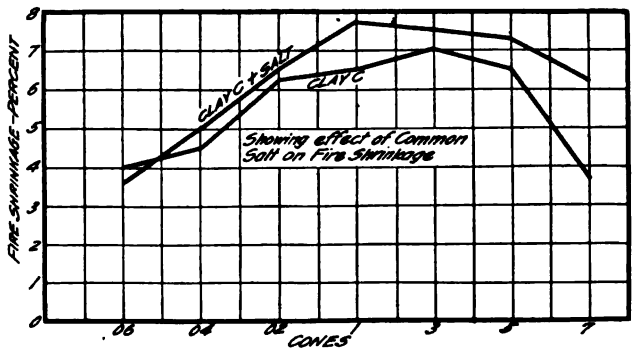
Prof. Staley: No. The cracking was reduced in all cases by the addition of sodium chloride and increased very decidedly by the addition of sodium carbonate.

Mr. Yates: This is a very desirable paper and very interesting to men of experience. It is skillfully gotten up, and I would like to ask Mr. Staley if his draft gauge showed the same circulation with the excessive amount of water? Straining on ware is a thing that has to be governed in such a manner that you cannot take the water off faster than it can exude from the center of the material.

Prof. Staley: These pieces were dried, not in a dryer, but simply in the laboratory, either close to the radiator or a far as we desired from it; however, all the pieces were made up at the same time and as nearly as possible in the same way, and if there


TRANS. AM. CER. SOC. VOL. XVII
FIG. 8.
STALEY
FIRE SHRINKAGE - PERCENT
CLAY A + SALT
CLAY A
Showing effect of ½% of Common Salt on Fire Shrinkage


FIRE SHRINKAGE - PERCENT
CLAY B + SALT
CLAY B
Showing effect of Common Salt on Fire Shrinkage


FIRE SHRINKAGE - PERCENT
CLAY C + SALT
CLAY C
Showing effect of Common Salt on Fire Shrinkage
CONES

is any variation in the atmosphere or draft or any other condition the pieces were all subject to the same variation. This study intended to show the relative behavior of clays dried under exactly the same conditions.

Mr. Stover: Was the amount of shrinkage in your clays in the drying lessened by the addition of these salts? Didn't it give you a greater fire-shrinkage, or at least a greater amount of moisture to drive off in your firing, and a tendency to greater total shrinkage?

Prof. Staley: Both sodium chloride and sodium carbonate lengthened the vitrification zone of the clay, that is, the clay would start to vitrify at a lower temperature but did not overburn until we reached the temperature at which the untreated clay overburned. If you can buy sodium chloride rather cheap, outside of any effect on drying, it would pay in the case of sandy clays at least to use a small amount of it, rather than fire to a higher temperature in order to get the density of the ware you desire.

Mr. Bleininger: I would like to ask just how accurate these results are in regard to the rates of drying? We have done work of this sort and found it very difficult to control the drying conditions, even from day to day. In fact we are now considering putting in a refrigerating device for cooling the air to a very low temperature and controlling the humidity.

Prof. Staley: As to that, I would say that the conditions of drying were not controlled accurately at all, but in any one series the clays were made up at the same time, and then allowed to sit in a damp box over night. The drying was started with all the samples in a given series at the same time, and if there was any variation in laboratory or room conditions, all the clays underwent the same variations. The variation had no very material effect on the rate of drying, as is shown by the smoothness of the curves. These curves are not rounded up at all. They are a series of straight lines drawn from point to point, and they are remarkably smooth for curves made in that way. They are actual results, not curves drawn through the mean of a lot of points.

Mr. R. J. Montgomery: I might say that the humidity in the atmosphere decreases during the day; that is, it will be high in the morning and will reach the lowest point about two o'clock in the afternoon. The variation during the day may be anywhere from 10 percent to 40 or 50 percent, depending upon weather conditions. If a drying test was started in the morning, the rate of evaporation would be slow, gradually increasing as the day advanced and finally decreasing again in the evening. This variation will without doubt, affect the slope of the drying curves, and it is highly probable that a constant drying time for all clays will not hold for all variations of humidity. Constant humidity conditions should be maintained throughout the test.

Prof. Staley: The fact of it is, of course, that the humidity conditions would affect the shape of the curves to some extent, but would not affect the relative shape of the curve to any extent. If it were more damp for sample No. 1 in the morning than in the afternoon, it would be more damp for sample No. 6 or 7 or any of the others. As far as accuracy is concerned, there is a great deal more chance for getting comparative results in an accurate manner if one makes up all the samples in a series and puts them all through the same process at the same time, than if he tries to run one through a dryer one week or one day and starts in the next week or next day to make and dry another sample. In the latter case, absolute control of drying conditions would be imperative, and we all realize the difficulties involved in maintaining such control.

TABLE I—EFFECT OF SODIUM CHLORIDE ON RATE OF DRYING
IOWA LOESS CLAY

No.	NaCl	HOURS DRYING								LINEAR SHRINKAGE	CRACKS
		0	4	16	28	44	92	116	140		
		PERCENT OF WATER									
	percent									*percent*	
0 L	0	21.75	19.32	15.65	12.92	10.41	4.65	3.86	3.46	5	3
1 LS	0.25	21.65	19.20	15.72	13.43	11.00	5.07	3.98	3.58	5	3
2 LS	0.50	22.00	19.58	15.81	13.76	11.63	5.62	4.65	4.17	5.5	1
3 LS	1.00	21.78	19.52	16.25	13.78	11.83	6.18	5.34	4.72	5.75	0
4 LS	1.50	21.75	19.47	16.39	13.90	11.94	6.62	5.56	5.12	6.0	0
5 LS	2.00	21.03	18.80	15.95	14.45	12.24	7.76	6.70	6.11	6.0	0

TABLE II—EFFECT OF SODIUM CARBONATE ON RATE OF DRYING
IOWA LOESS CLAY

No.	Na_2CO_3	HOURS DRYING								LINEAR SHRINKAGE	CRACKS
		0	4	16	28	44	92	116	140		
		PERCENT OF WATER									
	percent									*percent*	
0 L	0	21.75	19.32	15.65	12.92	10.41	4.65	3.86	3.46	5	3
1 LC	0.125	22.57	18.96	14.85	12.91	10.31	4.44	3.51	2.10	5	3
2 LC	0.25	22.19	19.70	16.12	13.13	10.94	4.97	3.58	3.08	4.5	5
3 LC	0.375	22.47	19.96	16.35	14.24	11.53	5.11	3.11	2.61	4.25	8
4 LC	0.50	22.10	19.40	16.02	13.53	11.34	5.25	3.28	2.69	4.0	11
5 LC	1.00	22.00	19.40	16.03	13.97	11.94	4.92	2.67	2.03	4.0	14

TABLE III—EFFECT OF SODIUM CHLORIDE ON RATE OF DRYING

DAKOTA JOINT CLAY

No.	NaCl	HOURS DRYING														LINEAR SHRINKAGE	CRACKS
		0	3	9	13	19	25	30	45	53	73	98	123	150	190		
		PERCENT OF WATER															
	percent															*percent*	
0	0	30	28.30	25.48	23.52	21.00	18.67	17.03	13.26	11.94	8.85	6.63	5.37	4.16	3.50	10	4
1	0.25	30	28.60	25.65	23.10	21.25	18.67	17.22	13.72	12.27	9.33	7.10	6.00	4.52	4.05	10	2
2	0.50	30	28.62	25.42	23.60	21.64	19.38	17.81	14.64	13.20	10.52	8.25	6.76	5.16	4.80	10½	1
3	1.00	30	28.74	25.80	23.90	21.80	19.65	18.00	14.67	13.50	11.08	9.05	7.62	6.05	5.60	10	0
4	2.00	30	29.00	26.10	24.45	22.25	20.28	18.67	15.90	14.52	12.23	10.25	9.00	7.42	7.35	10	0

TABLE IV — EFFECT OF SODIUM CARBONATE ON RATE OF DRYING

DAKOTA JOINT CLAY

No.	Na_2CO_3	HOURS DRYING														LINEAR SHRINKAGE	CRACKS
		0	3	9	13	19	25	30	45	53	73	98	123	150	190		
		PERCENT OF WATER															
	percent															*percent*	
J	0	30	28.30	25.48	23.52	21.00	18.67	17.03	13.26	11.94	8.85	6.63	5.37	4.16	3.50	10.10	4
1 JC	0.25	30	28.65	25.21	23.85	21.68	19.37	17.67	14.45	12.62	9.35	7.00	5.56	4.28	3.45	9.50	5
2 JC.	0.50	30	28.25	25.65	23.20	20.80	18.55	17.00	13.60	12.21	8.94	6.78	5.12	3.82	3.06	9.00	7
3 JC	1.00	30	28.25	26.74	24.93	22.46	20.01	18.29	14.84	13.40	9.95	7.27	5.52	4.02	3.15	....	14
4 JC	2.00	30	28.50	26.80	24.92	22.40	20.15	18.65	15.50	14.25	11.15	8.90	7.15	5.40	3.87	....	15

TABLE V—EFFECT OF MAGNESIUM SULPHATE ON RATE OF DRYING

WOODWARD SHALE

No.	$MgSO_4$ $7H_2O$	HOURS DRYING														LINEAR SHRINKAGE	CRACKS
		0	2	12.5	17.5	20	22.5	27.5	31	37.5	55.5	61.5	65	91	105		
		PERCENT OF WATER															
	percent															percent	
0 W	0	27.00	25.05	17.51	15.54	14.32	13.39	11.80	10.68	9.37	5.54	4.80	4.14	2.37	1.90	6½	0
1 WM	1	27.00	25.20	20.82	18.67	17.00	16.25	14.60	13.50	11.95	7.37	6.39	5.64	3.25	2.60	6½	0
2 WM	2	27.00	25.21	20.84	18.68	17.46	16.24	14.48	13.37	11.83	7.52	6.63	6.30	3.98	3.43	6½	0
3 WM	3	27.00	25.00	20.85	18.60	17.05	16.40	14.78	13.67	12.20	8.62	7.95	7.62	5.64	5.08	6½	0

TABLE VI—EFFECT OF CALCIUM SULPHATE ON RATE OF DRYING
WOODWARD SHALE

No.	$CaSO_4 2H_2O$	HOURS DRYING														LINEAR SHRINKAGE	CRACKS
		0	2.5	12.5	17.5	20	22.5	27.5	31	37.5	55.5	61.5	65	91	105		
		PERCENT OF WATER															
	percent															*percent*	
0 W	0	27	25.05	17.51	15.54	14.32	13.39	11.80	10.68	9.37	5.54	4.80	4.14	2.37	1.90	6½	0
1 WC	1	27	25.20	18.80	16.23	14.63	13.88	12.20	11.22	9.60	4.80	4.20	4.00	2.70	2.25	6½	0
2 WC	2	27	25.00	17.22	14.80	13.51	12.75	11.35	10.27	8.65	5.08	4.54	4.05	2.72	2.32	5½	0
3 WC	3	27	24.64	14.90	12.02	11.10	10.51	9.25	8.59	7.43	4.70	4.20	4.00	2.82	2.60	6	0

TABLE VII—SHOWING EFFECT OF SALT ON ABSORPTION

CLAY A		CLAY A + ½ PERCENT COMMON SALT	
CONE	ABSORPTION	CONE	ABSORPTION
	percent		*percent*
06	8.3	06	8.3
04	6.3	04	5.4
02	5.0	02	3.2
1	4.2	1	2.3
3	3.8	3	2.2
5	3.6	5	1.4
7	4.8	7	4.7

CLAY B		CLAY B + ½ PERCENT COMMON SALT	
CONE	ABSORPTION	CONE	ABSORPTION
	percent		*percent*
06	8.5	06	7.6
04	7.2	04	5.8
02	5.2	02	4.3
1	4.1	1	2.3
3	4.1	3	2.2
5	3.2	5	1.6
7	4.5	7	4.2

CLAY C		CLAY C + ½ PERCENT COMMON SALT	
CONE	ABSORPTION	CONE	ABSORPTION
	percent		*percent*
06	9.0	06	8.7
04	6.8	04	6.4
02	5.2	02	4.5
1	4.0	1	2.9
3	3.9	3	1.8
5	2.3	5	1.2
7	4.1	7	3.3

TABLE VIII—SHOWING EFFECT OF SALT ON FIRE SHRINKAGE

CLAY A		CLAY A + ½ PERCENT COMMON SALT	
CONE	BURNING SHRINKAGE	CONE	BURNING SHRINKAGE
	percent		*percent*
06	2.5	06	2.5
04	3.7	04	4.7
02	4.5	02	5.5
1	4.5	1	5.7
3	4.4	3	6.6
5	4.5	5	6.5
7	4.0	7	4.6
CLAY B		CLAY B + ½ PERCENT COMMON SALT	
CONE	BURNING SHRINKAGE	CONE	BURNING SHRINKAGE
	percent		*percent*
06	2.8	06	3.8
04	3.2	04	4.3
02	4.8	02	5.7
1	5.3	1	6.4
3	5.6	3	6.7
5	5.0	5	6.0
7	3.8	7	5.0
CLAY C		CLAY C + ½ PERCENT COMMON SALT	
CONE	BURNING SHRINKAGE	CONE	BURNING SHRINKAGE
	percent		*percent*
06	4.0	06	3.6
04	4.5	04	5.0
02	6.2	02	6.5
1	6.5	1	7.7
3	7.0	3	7.5
5	6.5	5	7.3
7	3.7	7	6.2

A METHOD FOR THE TITRATION OF CALCIUM OXIDE OR HYDROXIDE IN THE PRESENCE OF SOME ALUMINATES OR SILICATES[1]

BY WARREN E. EMLEY

Some investigations of sand-lime brick which are now under way, made it necessary to be able to determine, with a fair degree of accuracy, the amount of free lime contained in the material. Sand-lime brick consists essentially of sand, bound together by a hydrated calcium silicate, and it was desired to learn just what this calcium silicate is. The bricks are made commercially by mixing about 85 parts of sand with 15 parts of hydrated lime, and treating them with high pressure steam — generally 120 pounds for 10 hours. In order to prepare the silicate for laboratory investigations, it was found convenient to mix pure freshly burned and hydrated lime with washed and finely ground flint, and cook the mixture in an autoclave. Obviously, it is very difficult to determine the proportions, the pressure and the time, so that all of the lime will combine with all of the flint. There will generally be an excess of either one or both of the reagents remaining in the free state, as can readily be observed by the microscope. In order to make a quantitative analysis of the silicate, it is necessary to be able to distinguish between the free lime and that combined with the silica, or between the free flint and that combined with the lime.

An analytical method for determining free lime in the presence of calcium silicate might be of value for plant control. The free lime present in the brick would afford a means of juding the efficiency of the mixing machines, and might prove of assistance in determining the quality of sand to use, the steam pressure required, and the duration of the cooking.

There are also a number of problems confronting the lime manufacturer which could be attacked with greater assurance if such an analytical method were available. For instance, a compound is now on the market to be added to hydrated lime, in or-

[1] By permission of the Director, Bureau of Standards.

der to improve its plasticity. This compound consists essentially of calcium aluminate. The inventor claims that it enters into a chemical combination with the lime, and that, therefore, it should be added in a certain fixed proportion. It would be interesting to know if the chemical combination really does take place, and if so, to what extent.

The measurement of the causticity of lime as carried out for the technical control of a water softening plant might be put on a surer basis, if such a method were available.

The silicates and aluminates with which we have to deal are the salts of weak acids with a strong base. They are hydrolyzed quite readily, and show an alkaline reaction under ordinary circumstances.

Parr and Ernest[2] attempted to dissolve free lime in the presence of the calcium silicate found in sand lime brick, by treating the mixture with dilute acetic acid. Their experiments convinced them that this acid was too strong; that is, it hydrolyzed the silicate to some extent. By using a dilute solution of hydrogen sulphide in water, they claimed to be able to dissolve all of the free lime without decomposition of the silicate. In order to test this method, a sample of calcium silicate containing free lime was treated with hydrogen sulphide until all of the lime had dissolved. This point could be readily determined by the microscope, calcium oxide or hydroxide being easily distinguishable from the silicate on account of the differences in their indices of refraction. Further treatment of the same sample with hydrogen sulphide resulted in the solution of more lime, which can only be regarded as a direct refutation of the statement that hydrogen sulphide will not decompose the silicate.

The freshly prepared silicate, if suspended in water before it has had a chance to dry out, shows an alkaline reaction. If it is neutralized by dilute acid, its alkalinity will return too rapidly to make the attainment of a definite end-point possible.

These experiments led to the belief, that in order to titrate free lime in the presence of such a silicate, no acid, however weak, could be used, and the titration must be carried out in some medium other than water. In order to fulfill these con-

[2] *Bull. No.* 18, *Ill. State Geol. Sur.*

ditions, a number of experiments were tried, which finally resulted in the adoption of the following method:

In a 250 cc. flask, put 2 cc. of glycerine and 10 cc. of alcohol. Add the finely powdered sample in sufficient quantity to give about one-tenth of a gram of free lime. Add five drops of phenolphtalein solution. Bring to a boil, and keep near the boiling point throughout the titration. Titrate with $\frac{N}{5}$ alcoholic solution of ammonium acetate. The end point is reached when the pink color is discharged and does not return after boiling for one minute.

It was found that under the above conditions, ammonium acetate reacts with free lime, with the formation of calcium acetate (which is soluble in acohol) and free ammonia, which is removed as formed, by boiling. It is thus possible to eliminate both the acid and the water. Phenolphtalein was selected as the indicator, because it is soluble in alcohol, and because it is generally recognized as the best indicator for determining strong bases in the presence of weak acids[3]. Phenolphtalein is not very sensitive to fairly strong alkali in the presence of alcohol alone, and it is for this reason that the glycerin is used. The glycerin also helps to make the end point more definite, probably because of its ability to dissolve calcium oxide. Free ammonia impairs the sensitiveness of the indicator, and it is to prevent this that the titration is carried out in a boiling solution.

The following results of experiments will show to what extent the various silicates and aluminates are decomposed during the titration:

The solution of ammonium acetate was standardized by titrating a known weight of C. P. CaO, which was prepared as needed by calcining C. P. $CaCO_3$ to constant weight in an electric furnace. The first series of experiments were made by the writer, the second by Mr. J. C. Evans, of the chemical laboratory of the Bureau. The general method of procedure was to add a known weight of C. P. CaO to the sample to be examined, and then attempt to determine it by titration.

[3] Glaser, *Indikatoren der Acidimetrie and Alkalimetrie*, p. 96.

1. Standardization.

1ST SERIES.

Weight CaO taken = .2027 $NH_4C_2H_3O_2$ required = 33.76cc.
.2014 33.75cc.

Average = 1cc. $NH_4C_2H_3O_2$ = .00598 g. CaO.

2ND SERIES.

Weight CaO taken = .5008 $NH_4C_2H_3O_2$ required = 31.5 cc.
.1032 6.81cc.
.1407 9.1 cc.

Average = 1cc. $NH_4C_2H_3O_2$ = .0154 g. CaO.

2. Hydrated Mono-Calcium Silicate, $CaO:SiO_2:xH_2O$.

Prepared by precipitating a solution of $CaCl_2$ with Na_2SiO_3. The precipitate was purified by repeated washing, drying and grinding. By means of the microscope, it was finally found to contain about 5 percent $CaCO_3$, but no CaO or $Ca(OH)_2$. To about two-tenths of a gram of this material, C. P. CaO was added as follows:

	Wt. CaO added	Wt. CaO found
1st Series	.1014	.1046
2nd Series	.1119	.1109

3. β Dicalcium Silicate, β 2 CaO: SiO_2.

This material as well as all of the other silicates and aluminate tested, were prepared during some researches on Portland cement. They were examined microscopically by Mr. A. A. Klein, the petrographer of the Bureau, just before using, and found to contain no free CaO or $Ca(OH)_2$. To about one-half gram of this material, C. P. CaO was added as follows:

	Wt. CaO added	Wt. CaO found
1st Series	.1076	.1079
2nd Series	.0633	.0639

4. Tricalcium Silicate, 3 CaO: SiO_2.

This substance is slightly alkaline to the indicator. The color is readily discharged, but returns very slowly, so that a little practice is necessary in order to be sure of the end-point.

	Wt. 3CaO:SiO_2 taken	Wt. CaO added	Wt. CaO found
1st Series	.1000	.1003	.1002

5. Calcium Aluminate, $CaO : Al_2O_3$.

	Wt. $CaO : Al_2O_3$ taken	Wt. CaO added	Wt. CaO found
1st Series	.5000	.1032	.1032
2nd Series	.2000	.1430	.1445

6. Calcium Aluminate, $5\,CaO : 3\,Al_2O_3$.

	Wt. $5CaO : 3Al_2O_3$ taken	Wt. CaO added	Wt. CaO found
1st Series	.5000	.1116	.1071

7. Tricalcium Aluminate, $3\,CaO : Al_2O_3$.

In the presence of very small amounts of water, this material reacts alkaline to the indicator, and the alkalinity persists until sufficient lime has been neutralized to reduce the ratio to 5 $CaO \cdot 3\,Al_2O_3$. This is indicated by the following results:

	Wt. $3\,CaO : Al_2O_3$ taken	Wt. CaO liberated by reduction of $3\,CaO : Al_2O_3$ to $5\,CaO : 3\,Al_2O_3$	Wt. CaO added	Total CaO	CaO found
1st Series..	.5010	.1385	0	.1385	.1390
	.1993	.0552	.1012	.1564	.1538
2nd Series..	.2500	.0641	.1149	.1790	.1746

By taking particular precautions to have the alcohol and the glycerin as nearly free from water as practicable, Mr. Evans found that he could prevent the above reaction from taking place. Under these circumstances, the tricalcium aluminate does not react alkaline, and does not interfere with the determination of the free lime, as shown b the following results:

	Wt. $3\,CaO : Al_2O_3$ taken	Wt. CaO added	Wt. CaO found
2nd Series	.2500	.1149	.1149
	.2500	.1124	.1140
	.2500	.1141	.1130
	.2500	.1168	.1155

8. Calcium Carbonate, $CaCO_3$.

This was the C. P. material, which was dried on the hot plate before using.

	Wt. $CaCO_3$ taken	Wt. CaO added	Wt. CaO found
1st Series	.2000	.1020	.1021
	.2000	.1072	.1068
2nd Series	.5000	.1023	.1009

9. Plaster of Paris, $CaSO_4 : \frac{1}{2} H_2O$.

The ordinary commercial pottery plaster:

	Wt. $CaSO_4 : \frac{1}{2} H_2O$ taken	Wt. CaO added	Wt. CaO found
1st Series	.5000	.1048	.1056
2nd Series	.5000	.1132	.1149

10. Magnesia, MgO.

The grade known as "light calcined, technical," is neutral to the indicator, and does not interfere with the determination. After ignition it causes the formation of a very faint color, which returns so slowly that it does not seriously interfere with the end-point. The freshly ignited material was used in the following experiments:

	Wt. MgO taken	Wt. CaO added	Wt. CaO found
1st Series	.2000	.1015	.1000
2nd Series	.2000	.1081	.1070

11. Alca, (Technical Calcium Aluminate).

	Wt. Alca taken	Wt. CaO added	Wt. CaO found
1st Series	.5000	.1000	.0978
2nd Series	.2000	.1369	.1371

12. White Sand Lime Brick.

This was a commercial article, containing sand, calcium silicate, and calcium carbonate, but no oxide or hydroxide.

	Wt. brick taken	Wt. CaO added	Wt. CaO found
1st Series	.5000	.1075	.1046
2nd Series	.2000	.1112	.1124

Experiments were also tried with colored sand lime brick and with Portland cement, but without satisfactory results. The color of the material obscured the end-point of the reaction.

SUMMARY

By means of the method outlined, calcium oxide or hydroxide can be quantitatively determined, without difficulty, in the presence of the mono- or di-calcium silicates, the mono- or five to three calcium aluminates, calcium carbonate, or calcium sulphate. If tri-calcium silicate is present, the method is still applicable, but requires a little more skill in recognizing the end-point. The same remark is true to a less extent, if magnesia is present. With tri-calcium aluminate, especial precautions must be taken to insure the absence of water. The alcohol should be redistilled from quick lime immediately before using.

The method has afforded a satisfactory means of attacking the problems about sand lime brick and hydrated lime, and may perhaps find usefulness in other fields.

PROTECTIVE COATINGS FOR DRYER CARS[1]

BY M. C. BOOZE

The subject of protection for dryer cars is an important one to the ceramic manufacturer using waste heat dryers. The first cost of, and expense for repairs on the cars are large, so that the rapid corrosion of the metal means a fairly large loss to the owners.

The decks of the cars are made of soft, rolled steel channel bars of about $\frac{3}{16}$ inch thickness, five feet in length, and two inches wide, supported at both ends and in the middle. The corrosive action of the dryer gases is so great that the bars become rusted out within a year's time, and are not able to carry the weight of a load of dry clay without bending or breaking. In extreme cases, these bars have disintegrated within a period of six months.

Realizing the economic value to be gained by the clay operator in prolonging the life of the dryer cars, the following data by others on the corrosion of iron and steel and protective coatings is given, together with tests by the writer upon coatings which seemed to be the most promising.

There has been a wealth of material written upon the causes of corrosion and the means of protection against it. Instances are many, where one writer makes a statement in contradiction to another. In the following, an attempt has been made to quote from the more recognized authorities, and to accept results where the majority of the writers came to the same general agreement. Results proved by experiment were, in every case, given preference over theoretical ideas.

AGENTS CAUSING FAILURE OF THE IRON AND PROTECTIVE COATINGS

These may be divided into two classes, first, chemical agents and second, physical agents.

[1] A thesis under the direction of Prof. R. T. Stull, University of Illinois, 1915.

The chemical action is the more important, since it is the more injurious. The agents under this head are liquid and gaseous acids, and oxygen.

The physical agents to be considered are heat, jars from falling bricks, etc., and abrasion by friction.

Sulphurous acid is by far the most important acid to be considered[2]. Carbonic acid may be present in the dryer gases, but its corrosive action is not to be compared with that of the former. The sulphurous acid is formed from the sulphur dioxide obtained from coal burned in the kilns, and water vapor from the wet clay. It is deposited upon the cars after condensation of the water vapor in the dryer gases, and thus begins its action.

Sang[3] states that of all the agents in the air which accelerate rusting, especially near cities where much fuel is consumed, sulphur dioxide and soot are the most destructive.

Since the carbonic acid in the open air does not readily corrode a steel structure the sulphurous acid is evidently the more active acid, and hence, is the only one which will be considered.

The physical agents, in general, aid only in the failing of the protective coating. Heat accelerates the action of the acids upon the iron, and causes a physical change in some paints, such as cracking and brittleness in an oil paint, and softness in an asphaltic coating.

Jars and blows from falling bricks, etc., to which the cars are always subjected, chip off a brittle coating and predetermine the failing of an enamel or other hard and brittle covering. The paints are contantly subjected to abrasion through hard clay bodies sliding upon the surface of the cars, and ability to withstand such wear is a necessary quality of a satisfactory coating.

Rust begins at any spot where the metal is not covered, and spreads over the surface of the iron in all directions. It clings very weakly to the surface of the metal, and as a result, scales off easily—taking the paint with it and exposing an unprotected surface.[4]

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[2] Kent, *"Journal of the Franklin Institute,"* vol. 99, p. 437.
[3] *"Corrosion of Iron and Steel,"* p. 62.
[4] *"Protective Coatings for Iron,"* by Boennrath, p. 4.

Spennrath[5] states that rust aids the further formation of rust, through being porous and holding water and corrosive agents in contact with the surface of the iron.

Structural material coming from the mill is usually coated with an oxide called mill scale which adheres firmly to the surface of the metal. It is very often the case, that paint is applied over this scale. If the material has stood for any length of time before being painted, moisture has penetrated the scale and begun invisible corrosion[6]. This continues under the paint, until the scale becomes loosened from the underlying metal and falls off, which usually happens within a period of three or four months. Sang[7] states, that iron in contact with mill scale, when exposed to the atmosphere rusts about fifty percent faster than the bare metal.

The scale is often removed before painting by allowing rust to form, then cleaning the surface with wire brushes or a sand-blast[8 9 10].

Previous experiments have shown that oxygen and water vapor alone are not active in producing rust.[11] However, very small quantities of carbonic, sulphuric, or sulphurous acids cause rapid corrosion of iron and steel.[12]

Three theories have been advanced concerning the formation of rust:

1. The carbonic acid theory founded upon investigations by Calvert who asserts that carbonic acid is necessary in the formation of rust. This theory is disproved by several men,[13] who showed that rusting takes place very rapidly in the absence of carbonic acid.

2. The peroxide theory advanced by Traube. This has to do with the oxidation of iron by hydrogen peroxide. It is discredited by nearly all authorities on corrosion.

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[5] *"Protective Coatings for Iron,"* p. 20.
[6] Friend's *"Corrosion of Iron and Steel,"* p. 251.
[7] *"Corrosion of Iron and Steel,"* p. 80.
[8] Friend's *"Corrosion of Iron and Steel,"* p. 251.
[9] *"Technology of Paint and Varnish,"* by Sabin, p. 190.
[10] *"Corrosion and Preservation of Iron and Steel,"* by Cushman and Gardner, p. 121.
[11] *"Corrosion and Its Prevention,"* by Newman, p. 17.
[12] *"Corrosion and Its Prevention,"* Newman, p. 23.
[13] Goulding in *"The Journal of the Chemical Society of London,"* 1905; Cribb in *"The Analyst"* for 1905; and Whitney in *"The Journal of the American Chemical Society"* for 1903.

3. The electrolytic theory. This assumes that before the iron can oxidize, it must pass into solution as a ferrous ion. This theory is now accepted by nearly all writers. It is treated conclusively by Cushman and Gardner.[14]

By its means, every phenomenon connected with the rusting of iron can be satisfactorily explained. Thus the rapid corrosion of the dryer cars can be understood, when it is noted that such an electrolyte as sulphurous acid is present in the dryer, and is dissolved in the water that condenses upon the cars.

The electrolytic theory is too long to be fully discussed here. Excellent material upon the subject may be found in Cushman and Gardner's *"Corrosion and Preservation of Iron and Steel," "The Corrosion of Iron and Steel"* by Sang, and *"The Corrosion of Iron and Steel"* by Friend. Specific instances of electrolytic action are cited in *"Rustless Coatings"* by Wood.

The rate of corrosion is greatly affected by the physical condition of the metal.[15] Laminations in a piece of steel rust out much more quickly than the rest of the piece. The laminations are often due to cinder in the metal, which opens up the piece to the action of the corrosive agents. The cinder is acid in character and also directly aids the corrosion.

A state of stress or strain aids corrosion as do also bubbles or blow holes.[16] These strains are said by Sang[17] to be due to carelessness of manufacture. The rolling and cooling of the metal is carried on at such a high speed that the molecules are not given time to readjust themselve, and a strain is set up. Such strains are present in all commercial steel of to-day, and partially account for the fact, that modern structural material is more easily corroded than that made several years ago when more care was taken with the manufacture. Jackson[18] states that the rate of corrosion increases practically in proportion to the strain. This accounts for the increased corrosion around rivet holes and sheared edges.

[14] *"Corrosion and Preservation of Iron and Steel,"* p. 56.
[15] *"Rustless Coatings,"* by Wood, p. 332 and 344.
[16] *"Corrosion and Preservation of Iron and Steel,"* by Cushman and Gardner, p. 2.
[17] *Proceedings of the Engineering Society of W. Pa.*, Vol. XXIV, p. 511.
[18] *Transactions of the American Society of Mechanical Engineers*, Vol. XXII.

CLASSES OF COATINGS AND RESULTS OF PREVIOUS TESTS UPON SOME PAINTS

The protective coatings may be divided into three classes:

1. Paint coatings, including linseed oil paints, varnishes, lacquers, bitumens, cements, and enamels.

2. Magnetic oxide surfaces.

3. Coatings of other metals.

The cheapest and most common paint used is one containing linseed oil as a vehicle. Investigations by Spennrath[19] however, show the futility of using an oil paint under the conditions found in a waste heat dryer. He used graphite as a pigment in these tests, and pure, boiled linseed oil as a vehicle. Since the graphite was perfectly inert and unaffected by the chemical agents present, any failure was undoubtedly due to the oil.

Several paints, each containing a different percentage of linseed oil, were exposed to a temperature of 203 degrees Fahrenheit for several days, and in each case, the paint became stiff and brittle and shortened from 3 to 4 percent. A coating of the same material was suspended over a solution of gaseous sulphurous acid. It was destroyed within a few days and passed off in drops.

Spennrath states that there is no remedy against the injurious influences attacking the binding material.

In several paint tests in which the paints were exposed to the influences of sulphurous acid gases and weathering conditions, it was found that asphaltic paints and compounds of rubber lasted very poorly.[20]

Cushman and Gardner[21] state that railroad tunnels, whose atmosphere is rich in sulphur dioxide, carbonic acid, and moisture, call for the very best inhibitive paints that it is possible to design. In train sheds, in which the girders were constantly surrounded with smoke from the locomotives, the only satisfactory paint found was a linseed oil varnish. No other paint had

[19] *"Protective Coatings for Iron,"* p. 21.
[20] *Engineering News,* Vol. 148, p. 164.
[21] *"Corrosion and Preservation of Iron and Steel,"* p. 218.

the ability to long withstand the corrosive agents. The heat in a waste hat dryer prohibits the use of such a coating for dryer cars.

Tar paints were also found to fail completely in a position where they were continuously surrounded with coal smoke.[22] Tar coatings are seldom if ever pure and produce rust through the acetic acid that they contain.[23]

Asphalt must be pure to be used in paints. In this state, it is costly. It also becomes hard and brittle when cold and cracks easily. It is easily weathered by atmospheric influences.

Rubbing down with graphite has been practiced in some cases. Spennrath[24] states that this is of little value since it is impossible to completely cover the surface and the metal soon corrodes.

Organic fats produce rust through the fatty acids that they contain.

Varnishes are composed of resins dissolved in linseed oil. Since sulphurous acid so vigorously attacks the oil, such coatings would be useless.

Lacquers were found by Walker[25] to actually stimulate corrosion when acids were present. They are also porous and allow the penetration of aqueous solutions.[26]

Baked japan coatings composed of pure bituminous matter dissolved in gum or oil should afford an excellent means of protection and will be tested.

Paint enamels are mixtures of varnishes with metallic pigments. Hence they are to be classed with varnishes or oil paint.

Certain cements whose bonding power relies upon the setting of some of the ingredients may be valuable and will be tried.

Portland cements are the best means of protection against rusting that are known. Where the metal is not liable to wear or jars a wash of Portland cement gives adequate protection.

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[22] *"Iron Corrosion,"* by Andes, p. 117.
[23] *"Technology of Paint and Varnish,"* by Sabin, p. 185.
[24] *"Protective Coatings for Iron,"* by Spennrath, p. 35.
[25] *"Journal of Industrial and Engineering Chemistry,"* 1909, p. 754.
[26] *"Corrosion and Preservation of Iron and Steel,"* by Cushman and Gardner.

Certain oxides produced upon the surface of the metal prohibit corrosion under certain conditions. Iron boiled in potassium bichromate solution produces an oxide which inhibits rusting under atmospheric conditions. The oxide, however, loses this passivity in the presence of aqueous acids and on heating.[27] Russia iron owes its ability to withstand rusting to an oxide coating which is produced by the action of steam at a high temperature. This scale is brittle and may be broken or worn off. It is also expensive to produce. It is of advantage, as a protection against corrosion, to produce upon the surface this passive oxide and then paint over it. Rusting will not take place for some time after the paint has been removed, so that small spots exposed by wearing away of the paint may be repainted. Where paint is applied to the bare metal, it is not advisable to touch up worn places with new paint because rusting has undoubtedly taken place upon the exposed metal and spread for some distance under the surrounding paint. Covering up the rust only hides its action. Whenever the paint has been broken away in several places, the whole surface should be cleaned and recoated.

Fraudulent Paints. In order to increase sales, many companies advertise their paints as having properties which it is impossible for them to possess. Andes[28] refers to such paints as follows:

"When we read in a manufacturer's circular that he has invented and prepared a paint that is capable of destroying pre-existing rust, and thereby of preserving rusted iron from any further encroachment, it is evident that such a claim is an impossibility. If another maker avers that his product possesses magnetic or electrical properties, this is an absurdity, because any pigment ground up in, and therefore surrounded by, linseed oil or linseed varnish is thereby rendered altogether inert. Another manufacturer claims as an advantage for his paint that the pigment he uses, unlike those of others, does not undergo saponification with the oil in the varnish and therefore must be more durable. It is well known that no saponification occurs in paint and that the durability of a paint may be reduced by the action of an oxidizing pigment (red or white lead) on the oil or varnish, whereas an inert body exerts no action. Furthermore, in many instances, totally unjustifiable claims are put forward on behalf of certain pig-

[27] "*Corrosion of Iron and Steel*," by Sang, p. 97.
[28] "*Iron Corrosion and Anti-Corrosive Paints*," p. 115.

ments such as iron oxide or graphite in the form of scales quite visible to the naked eye. It is asserted that in these paints, the individual flakes are completely enveloped in varnish and lie one above another so as to actually form a number of coats of paint in one. If, however, the scales be examined through a magnifying glass, they will be apparent as coarse, granular fragments with only a few lustrous plates. Hence the pignent cannot produce any such coating as is claimed."

The latter, commonly called scale armor paint, has been greatly advertised as a protective coating. It is shown by Spennrath to be of no more value than any oil paint. He also disclaims the value of any paint said to have electrical or galvanic action.

Certain pigments used in paints are active in producing rust. Wood[29] explains their action as being to dissolve portions of the iron, and to deposit the metal which they contain upon the surface of the iron. These deposits excite galvanic action and cause corrosion and pitting. Both mercury and copper salts are offenders in this way. Also salts of lead, antimony, tin, silver, carbon, and manganese are detrimental, if they come in contact with the iron through decay of the paint film.

METAL COATINGS

The metal coatings applied to iron are usually of nickel, zinc, lead, copper, or tin.

Lead and tin offer little or no protection. Iron plates coated with either of these metals rust in a very short time. Nickel must be over .02 of an inch thick to give an adequate protection. Iron dipped in molten zinc forms an alloy with the zinc and gives the most effective of all metallic coatings.[30]

Copper is said to promote rust through galvanic action upon the iron.[31] At least, it does not provide an adequate protection.

PREPARATION OF THE SURFACE BEFORE PAINTING

Too much emphasis cannot be given the fact that the metallic surface to be protected must be absolutely clean and dry before applying the coating.

[29] "*Rustless Coatings*," p. 344.
[30] "*Protective Coatings for Iron*," Spennrath, p. 38.
[31] "*Rustless Coatings*," by Wood p. 344.

During storage, manufacture, etc., of the steel material, ample time is given for the formation of rust. Mulder states that "An iron article may remain bright for a long time but whenever any portion is attacked by rust, the latter will very quickly spread over the entire surface." Mill scale is also present upon the surface. Its effect has already been discussed.

Andes[32] comments upon the effect of rust as follows:

"Rust is, from the outset, the most powerful antagonistic influence to the resistent capacity of the succeeding paint, unless it is entirely removed before the latter is applied."

We know that the presence of rust is favorable to the further production of rust, since it contains moisture derived from the air, and also that rusting can take place under the paint film. The bond between rust and iron is very slight. and no paint can be expected to adhere to or protect a corroded surface.

There are three methods of cleaning the surface. They are by pickling, scraping, or sand-blasting.

In the first method, the metal is immersed in a 10 to 20 per cent solution of sulphuric acid and allowed to remain until the rust or scale loosens and falls off. This process is very efficient for cleaning the surface, and requires only about twenty minutes for the process, but many objections are registered against it on account of the difficulty in washing off the acid. Should any of the acid remain, it will produce additional rust. The effect of any acid remaining, however, may be counteracted by washing in a bath of milk of lime. If correctly carried out, this method is the cheapest and most efficient for removing rust or scale.[33]

Scraping off the rust is accomplished by means of wire brushes which are rubbed against the surface. This does not remove the rust from pit-holes nor is it economical. Sand blasting is a very cheap and quick method for cleaning iron. It requires, however, suitable apparatus with air under pressure and so is not suitable to every plant.

The paints should be applied immediately after cleaning the iron.[34] Rust forms very quickly and easily upon a clean iron

[32] *"Iron Corrosion and Anti-Corrosive Paints,"* p. 58.
[33] *"Corrosion and Its Prevention,"* by Newman, p. 130.
[34] *American Society for Testing Materials*, Vol. V, p. 436.

surface and, should the metal be allowed to stand in the atmosphere before painting, a small amount of moisture will condense upon the surface, causing some rust to form and preventing the perfect adherence of the protective coating.

Paints if applied to a hot metal surface afford greater protection through rapid drying and complete absence of moisture. This method has been practiced in painting ships by admitting steam into the hold and heating up the metal sides just before painting. Paints applied under these conditions have shown increased lasting qualities.

Oil or grease upon the surface of the iron prevents the paint from sticking and so is a detrimental factor.

PAINTS TESTED IN THIS WORK AND RESULTS OF THE TESTS

It is evident that the use of several paints, varnishes, and other coatings is precluded. Those whose values have not been determined are acid proof cements baked japan coatings, and commercial paints whose composition is unknown.

Concerning the latter, about twenty of the larger paint companies were asked to submit samples of their paints to be tested under dryer conditions. Only three paints were obtained. These were The Southern Cotton Oil Company's metal coat No. 27, protective enamel No. 6 from The General Bakelite Company, and Toch Brothers' No. 44 R. I. W.

The fact that only three concerns had paints for use under the conditions of a waste heat dryer, shows the difficulty of obtaining any suitable coating. Nearly all of these companies have paint specialists and research laboratories employed for the purpose of discovering suitable protective coatings for use under such severe conditions as are present in this case. In the majority of cases, these inquiries were referred to these research laboratories, and the answers were, as a rule, very discouraging in that no paints were known which could be recommended for such a purpose.

In addition to the above paints, aluminum bronze paint and

bicycle paint were thought to be feasible. Aluminum bronze paint is used in chemical laboratories to some extent for protecting iron pipes gainst the action of acid fumes. A commercial sample was obtained for the test. The bicycle paint was made up with the following ingredients: oil of tar, 4 parts; pure asphaltum, 1 part; and powdered resin, 1 part.

Two cements were made up; the first containing 100 parts of india rubber softened by heat, 6 parts of tallow, dry slaked lime added until the mixture assumed the consistency of a soft paste, and lastly about 20 percent of red lead was added to make it dry and harden. The second cement was made of 3 parts of barium sulphate mixed with 2 parts of ground asbestos and 2 parts of sodium silicate.

The baked japan coating was made by melting 1 part of the mineral gilsonite and dissolving in 5 parts of turpentine.

In addition to these coatings, one plate was boiled in a solution of potassium bichromate, while another was coated with a linseed oil paint using white lead as a pigment. The latter was tested as a means of verifying previous results and as a comparison with the other coatings.

The plates used in the tests were of soft rolled steel, about five inches long, two and one half inches wide, and three sixteenths of an inch thick. They were cleaned by immersing in a 20 percent solution of sulphuric acid until all of the scale was removed, and then boiling in several changes of water until all of the acid was washed off. They were then quickly dried and placed in a desiccator containing calcium chloride, until ready for use.

All of the paints were applied by dipping with the exception of Toch Brothers' No. 44 R. I. W., which was put on with a brush. Three coats were applied in each case, and one coat was allowed to become thoroughly dry before applying another.

None of the coatings showed preliminary defects with the exception of the asbestos cement and the baked japan coating. The latter was very brittle after baking and was easily chipped off, while the cement was soft and could be crumbled and scarred with the finger nail.

When all of the coatings had become dry and hard, the plates were placed in an electric oven and kept at a temperature of 120 degrees Centigrade for two weeks.

The oil paint cracked and curled up within a few days.

Toch Brothers' No. 44 R. I. W. softened considerably at first, but gradually became harder and finally became almost brittle.

The india rubber cement became soft and sticky and remained so until the end of the heating period.

The asbestos cement did not change.

The Southern Cotton Oil Company's metal coat No. 27 became harder and adhered more firmly to the surface of the plate. It seemed to be in excellent condition at the end of the two weeks.

The bakelite coating was not at all affected.

The aluminum bronze coating became soft and sticky at first, but hardened after a few days baking.

The bicycle paint became fairly soft and did not harden upon further baking.

The baked japan coating did not change.

After the baking test, the plates were suspended in a closed vessel over a saturated solution of sulphurous acid, and water vapor was allowed to condense upon them. They were kept in this position for about two months, while fresh solutions of the acid were put in from time to time.

The Bakelite and Toch Brothers' coatings were not at all affected. There was no perceptible formation of rust.

The Southern Cotton Oil Company's metal coat No. 27 turned yellow in spots, becoming less elastic and rather easily scraped off the plate.

Corrosion was soon perceptible under the asbestos cement.

The rubber cement became hard and lost its bond with the plate, allowing the acid to reach the metal underneath.

Rust soon formed under the aluminum bronze coating, and it came off in scales.

The baked japan coating was not affected.

The bicycle paint lost its lustre and, upon jarring, loosened from the plate. It was found to have allowed the pentration of the acid solution since spots and lines of rust had been formed.

The plate boiled in potassium bichromate did not long withstand the action of the acid. The surface was covered with rust within a few days.

An unprotected plate was greatly rusted within twelve hours from the beginning of the test.

As a final test, the plate coated with Bakelite, Toch Brothers' No. 44 R. I. W., linseed oil paint, and The Southern Cotton Oil Company's metal coat No. 27 were partly immersed in the acid solution and allowed to stand for two weeks.

At the end of this time, the Bakelite and Toch Brothers' coatings were not affected except on the edges where the paint had not fully covered the metal.

The oil coating was rotten and could be easily scratched off.

The Southern Cotton Oil Company's metal coat No. 27 had completely disappeared where it had been covered with the acid solution.

RESULTS OF TESTS OF BRITTLENESS AND RESISTANCE TO FRICTION

As a means of testing the relative hardness or resistance to friction, a device was constructed which allowed clean quartz sand to fall upon the coated plates in streams about one-eighth of an inch in diameter, and from a heighth of three feet. The length of time required for the sand to wear through the coating to the steel plate was the basis of comparison. The thickness of the coatings was not measured. Since three coats of the paint just as prepared commercially should, and probably would, be applied in practice, tests upon paint films of equal thickness would not be of practical value.

The coatings were tested for brittleness or adhesiveness by dropping a two inch steel ball upon the coated plate from different heights. The plate was supported at both ends and the ball was dropped upon the center.

The results of the tests are shown in Table I.

TABLE I

COATING	HARDNESS Time required to wear through the coating.	BRITTLENESS Height from which the ball was dropped before coating was broken through.
Bakelite	11 hours	No cracks were developed when the ball was dropped from a distance of ten feet. The surface was only indented.
Toch Brothers' No. 44 R. I. W.	8 hours	The coating was crack completely off in spots when the ball was dropped only six inches.
Southern Cotton Oil Company's metal coat No. 27	4 and ½ hours	The coating did not crack but was considerably bruised when the ball was dropped from a height of six feet.

USE OF DIFFERENT MATERIAL IN THE CARS

Since the protection of the dryer cars is such a difficult problem, it should not be out of place here to discuss the use of other materials which are not so easily corroded as the type of steel commonly used.

While it is known that cast iron under certain conditions has a slower rate of corrosion than rolled steel, many writers assert that the former is more acted upon by acids than the latter. However, this is not the case in waste heat dryers. In at least three different cases, it was observed that the wheels and standards of the cars which were of cast iron, were very little affected by the gases while the slats of the decks, which were of rolled steel, were covered with a layer of rust of at least one-third of the original thickness of the bar. This resistance to corrosion is said to be due to both physical and chemical make-up and also to the fact that thin, siliceous skin is formed upon the surface of

the casting by contact of the molten metal with the sides of the mold.

The explanation given by Stead[35] for the resistance of cast iron to the action of sulphuric acid is that a thick, protective film of ferrous sulphate is formed upon the surface of the metal.

Friend[36] states that white cast iron resists the action of acids better than the gray variety, but the former is more brittle and would probably not be as valuable as the tougher, gray variety.

A grade of steel called ingot iron is now being made by the American Rolling Mills Company, of Middleton, Ohio, which is advertised as being much less liable to corrosion than ordinary structural material. Being a fairly new product, its true worth has not yet been definitely established. A dryer car of this material has recently been made for the Western Brick Company at Danville, Illinois, and is now being tried out in their dryer. The test has not been carried on long enough as yet to be of value. The cost of this non-corrosive steel is only about ten percent above that of the ordinary structural steel, so the use of the former would be justified should it lengthen the life of the cars to any extent. The analysis of ingot iron as determined by Friend[37] is as follows:

	percent
Sulphur	0.021
Phosphorous	0.005
Carbon	0.02
Manganese	trace
Silicon	trace
Iron (by difference)	99.954

Plates of this metal, of charcoal iron, and of ordinary steel were carefully polished and placed in a 25 percent solution of sulphuric acid at a temperature of 110 degrees Centigrade for a period of one and one-half hours. They were then removed cleaned, and weighed. The following results were obtained:

[35] *Journal of the Iron and Steel Institute*, 1908.
[36] "*Corrosion of Iron and Steel*," p. 117.
[37] "*Corrosion of Iron and Steel*." p. 114.

MATERIAL	LOSS IN WEIGHT *percent*
Steel	87.5
Charcoal iron	52.1
Pure ingot iron	2.16

In addition to the different types of metal such as cast iron, ingot iron, etc., there are many alloys of iron and steel which show different rates of corrosion.

Cushman[38] states that "In considering the corrosion of iron, it is important to remember that iron is a metal which readily combines with or dissolves nearly all of the other elements, and that very small quantities of impurities suffice to change entirely its physical properties or characteristics."

Nickel, cobalt, tin, copper, chromium, phosphorous, and silicon when alloyed with iron or steel, decrease the tendency toward rusting while aluminum, manganese, antimony, arsenic, sulphur, and carbon increase corrosion.[39] [40] [41] These impurities are never found uniformly dissolved in iron or steel so that a solid piece of metal may corrode much more rapidly in one place than in another.

While copper alone decreases rusting, it is usually found compounded with sulphur. The sulphide is easily oxidized and produces a corrosive acid so that copper may be considered as being a detrimental constituent unless the steel contains little or no sulphur.

Experiments carried out by The Carnegie Steel Company[42] show that Bessemer steel corrodes more rapidly than open-hearth steel, and that an acid open-hearth steel corrodes more rapidly than a basic open-hearth steel. It was also found that wrought iron corrodes more rapidly than steel in almost all cases, and that the higher the carbon in steel, other things being equal, the more rapid the corrosion.

In a paper upon "The Corrosion of Iron and Steel," Edward Crowe stated that phosphorous in steel was a very power-

[38] *"Corrosion of Iron and Steel,"* p. 9.
[39] *Iron and Coal Trades Review*, Vol. 78, p. 341.
[40] *"Corrosion of Iron and Steel,"* by Friend, p. 209.
[41] *"Corrosion of Iron and Steel,"* by Friend, p. 82.
[42] *"Corrosion of Iron and Steel"* by Sang, p. 57.

ful antidote to corrosion. Diegel[43] found by experiment that the corrosion of steel was in inverse proportion to the phosphorous content.

DISCUSSION AND CONCLUSION

It is evident that, with the exception of Bakelite, there are no very satisfactory coatings for use on dryer cars. The conditions under which the cars are used are probably the most severe to which a paint is ever subjected. Andes[44] says that "no paint will resist the action of smoky fumes evolved from coal fires, and it is as yet impossible—all promises to the contrary notwithstanding—to provide an efficient protection for iron bridges and other structures exposed to such influences."

By "efficient protection" is meant a protection which will increase the length of the life of the cars at least enough to pay for the application of the coating. Then, according to Andes, it is a waste of time and money to attempt the protection of dryer cars by means of any known coating. Whether this is true or not, it is impossible to say. It seems to be borne out, however, by all experience with such coatings. The tests upon the coatings, herein contained were merely relative, and nothing can be said concerning their life in actual praticc. Plates coated with the three commercial paints—Bakelite, Toch Brothers', and the Southern Cotton Oil Company's— were sent to the Western Brick Company at Danville, Illinois, to be tested in their dryer. Having been sent only a few weeks ago, nothing is known as yet of their practical value. The laboratory tests, however, indicate that Bakelite is the only one which will be of practical value. The paint from The Southern Cotton Oil Company fails in contact with sulphur dioxide and water, while Toch Brothers' paint is too brittle to be of any practical value. All are hard enough to withstand rather severe wearing conditions. The fact that Bakelite withstood, in an entirely satisfactory manner, the action of sulphurous acid, and that it had extreme hardness and tenacity, indicates that it would afford a truly efficient means of protection for dryer cars.

[43] *Iron and Coal Trades Review*, 1909, p. 341.
[44] "*Corrosion of Iron and Steel*," p. 117.

The cost of Bakelite in 400 pound lots is thirty-five cents per pound. The Southern Cotton Oil Company's metal coat No. 27 costs ninety cents per gallon. No prices were quoted on Toch Brothers' No. 44 R. I. W. The spreading value of Bakelite as given by the manufacturers is 110 square feet per pound for one coat, while that of the Southern Cotton Oil Company's paint is given as 300 square feet per gallon so that the cost per square foot is approximately the same.

Since the increased life of the cars is the vital point to be considered, the best must be made of a very difficult problem. On account of the high cost of steel and the expense of replacing rusted bars with new ones, it would seem that coatings lasting only two or three months would be of value. However, this can only be determined through practical experience. The life of the coating can be greatly lengthened by using extreme care in the preparation of the surface and in the application of the paint.

The use of cast or ingot iron seems to be the best solution of the problem. Cast iron is brittle and heavy, but with correct construction these difficulties could be cut down until they were more than offset by the higher cost and shorter life of the rolled steel.

Ingot iron is just coming into use. Should it prove as rust-resisting as advertised, it will make unnecessary the use of any protective coating.

Ceramic Laboratories,
University of Illinois,
Urbana, Ill.

MICROSCOPIC INVESTIGATION OF SOME COMPOUNDS NOTED IN THE SYSTEMS SODA-ZINC OXIDE-SILICA AND SODA-ZINC OXIDE-TITANIC OXIDE-SILICA[1]

BY A. A. KLEIN AND G. H. BROWN, PITTSBURGH, PA.

Crystalline glazes of widely varying compositions and maturing temperatures have been successfully used in the ceramic industries, and a paper dealing with the subject is limited to one portion of the field. As most of the previous work reported in the *Transactions* deals with the application of the glazes to bodies, disregarding the nature of the crystals themselves, it was thought that a petrographic examination of certain types of these glazes would be of interest.

A type of glaze which has been used successfully to some extent is a simple alkaline silicate in which one or more crystallizers are used to produce the crystalline effect.

In this paper, a petrographic examination of a portion of the field covering this type of glaze is reported, no attempt having been made to fit the glaze to a body in the production of ceramic ware.

Preparation. Each mixture was ground in an agate mortar and passed through an 80 mesh sieve several times to insure thorough mixing.

Burning. Owing to the excessive fluidity of some of the mixtures, the fusions were made in small unglazed porcelain crucibles holding about 5 cc. In this way, loss of part of the fusion by flowing away, as occurs on flat vertical surfaces, was obviated, and most of the material preserved. Furthermore, segregation as a result of flow and the resultant inhomogeneity of the melt was reduced to a minimum. Mixtures having about the same fusion points were fired in closed saggers to the requisite temperatures. The more fusible mixtures were burned in a down

[1] By permission of the Director, Bureau of Standards.

draft test kiln fired with natural gas. The more refractory mixtures were burned in closed saggers in a furnace fired with natural gas and compressed air, and the highly refractory ones in a gas-fired pot-furnace. After reaching the desired temperature and holding for one hour, the gas was shut off, and the furnace cooled. In this investigation, it was found that the size of the crystals was not materially affected by the rate of cooling, equally large crystals being developed by rapid and slow cooling.

Owing to the fact that the porcelain crucibles were unable to withstand the corrosive action of the more refractory mixtures, these fusions were made in platinum crucibles. Before examining the melts petrographically, the porcelain crucible was broken entirely away, leaving only that part of the melt which was comparatively free from contamination with it.

SODA—ZINC OXIDE—SILICA

The portion of the field, zinc oxide-soda-silica, investigated lay between the concentration, 60 percent ZnO, 40 percent SiO_2, 10 percent ZnO, 90 percent SiO_2; and 10 percent ZnO, 50 percent Na_2O, 40 percent SiO_2. Fusions were made of compositions denoted by the vertices of the small triangles of Fig. 1, so that the melts differed from adjacent ones by 5 percent of the constituents.[2] In addition, three series were prepared for more thorough study, in which the ratio of zinc oxide to soda was kept constant, and the silica varied. In the first series, the formulae may be represented by

$$\left.\begin{matrix} .7\ ZnO \\ .3\ Na_2O \end{matrix}\right\} X\ SiO_2;$$

in the second, by

$$\left.\begin{matrix} .8\ ZnO \\ .2\ Na_2O \end{matrix}\right\} X\ SiO_2;$$

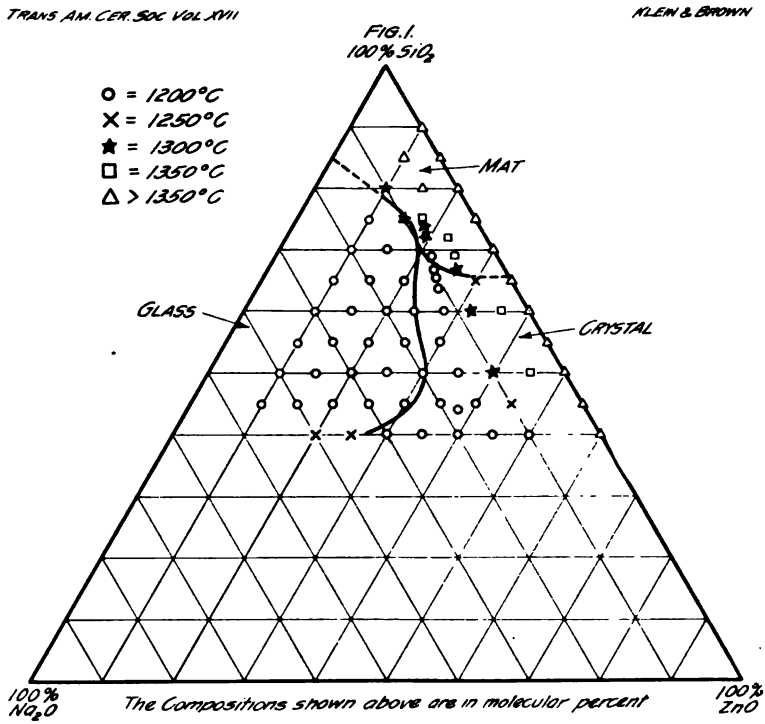
and in the third, by

$$\left.\begin{matrix} .9\ ZnO \\ .1\ Na_2O \end{matrix}\right\} X\ SiO_2,$$

in which X varied from 1 to 2.9 molecules. In Fig. 1, these have been calculated to molecular percentages.

[2] All percentages referred to in this work are molecular percentages.

Three types of structures were observed in the fusions:[3] crystal, mat and glass. In the crystal type, the crystals could be readily seen with the naked eye (megascopic) and were imbedded in a glassy groundmass. The mat type appeared dull opaque, stone-like to the eye, and the individual crystals could be seen only with the polarizing microscope. The glass type was isotropic and contained no crystals or crystal nuclei.



A number of interesting observations can be made from the study of Fig 1. Fusions containing a lower ratio of zinc oxide to soda than .6 molecules to .4 molecules will contain no crys-

[3] In this paper, the term "crystalline glaze" has been purposely avoided, and the terms "melt" and "fusion" used, since, while soda, zinc, silica, fusions may serve as the basis for crystalline glazes, these were not fitted to any body and might require changes in the formula before becoming a satisfactory glaze.

tals unless the content of silica is very great. In this case, the type of crystal has changed, as will be shown later.

When the silica content increases, the melts become more viscous, impeding crystallization. As a result, the crystals become smaller, and the melts show a mat structure.

Increasing either the silica or the zinc content produces a more refractory melt. The effect of the zinc is evidenced by comparing the following melts:

$$\left.\begin{matrix}35 \text{ percent. } ZnO \\ 15 \text{ percent. } Na_2O\end{matrix}\right\} 50 \text{ percent } SiO_2,$$

which requires a temperature of 1200° for maximum crystallization;

$$\left.\begin{matrix}40 \text{ percent } ZnO \\ 10 \text{ percent. } Na_2O\end{matrix}\right\} 50 \text{ percent } SiO_2,$$

which requires 1300°; and

$$\left.\begin{matrix}45 \text{ percent. } ZnO \\ 5 \text{ percent. } Na_2O\end{matrix}\right\} 50 \ SiO_2,$$

which requires 1350°. The effect of the silica is shown by comparing the following fusions:

$$\begin{matrix}35 \text{ percent. } ZnO \\ 15 \text{ percent. } Na_2O\end{matrix} \quad 50 \text{ percent } SiO_2,$$

noted above, with

$$\left.\begin{matrix}17.5 \text{ percent. } ZnO \\ 8.0 \text{ percent. } Na_2O\end{matrix}\right\} 74.5 \text{ percent } SiO_2.$$

Calculating the R O to 1 the formulae become

$$\left.\begin{matrix}.7 \ ZnO \\ .3 \ Na_2O\end{matrix}\right\} 1 \ SiO_2, \text{ and}$$

$$\left.\begin{matrix}.7 \ ZnO \\ .3 \ Na_2O\end{matrix}\right\} 2.9 \ SiO_2$$

respectively. The former requires a temperature of 1200°, as compared with 1350° for the latter.

There has been but one type of zinc compound to whose crystallization the crystalline and mat structures are due. This compound is noted in long, prismatic needle crystals, and the cross section, wherever it can be obtained, is hexagonal. (See

Figs. 2, 3 and 4.) It occurs irregularly disseminated in the glassy groundmass; it may exhibit parallel grouping or the individuals may radiate from a common nucleus, giving rise to what are known as radial spherulites. Under the microscope, the crystals often show excellent cleavage parallel to the prismatic C axis. The extinction is parallel to the cleavage, and a fairly high double refraction is noted, second order interference colors being prevalent. The indices of refraction for sodium light as determined by the immersion method are $\eta_o = 1.695 \pm .002$ and $\eta_e = 1.715 \pm .002$. $\eta_e - \eta_o$ (measured) $= .019 \pm .003$. The

FIG. 2

FIG. 3

c axis is the direction of the slow ray, hence the principal zone is $+$. The interference figures on the prism faces are apparently biaxial, but those of the terminal face orientated perpendicular to c are uniaxial, and the optical character is positive. The anomaly of uniaxial crystals orientated parallel to c showing apparently biaxial interference figures with large optic axial angles has been noted previously. The optical constants of this compound are practically identical with those of willemite, whose composition is $2\,ZnO.SiO_2$. According to Gaubert,[4] the refrac-

[4] Groth, *Chemische Krystallographie*, II, p. 253.

tive indices of natural willemite are $\eta_o = 1.6931$ and $\eta_e = 1.7118$. However, owing to the acidity of the fusions it seemed remarkable that zinc orthosilicate ($2\ ZnO.SiO_2$) should separate out from the melts instead of zinc metasilicate ($ZnO.SiO_2$). Moreover, according to Van Klooster[5] and Endell,[6] zinc metasilicate crystallizes in hezagonal prisms, showing uniaxial positive interference figures. No data concerning refractive indices were given. Endell states further, that the crystals of zinc crystalline glazes are likely those of zinc metasilicate.

Accordingly, fusions were made of both zinc ortho- and metasilicate and examined optically. The zinc orthosilicate fusion was practically homogeneous and its crystals possessed the optical constants given above. Zinc metasilicate was never obtained in a condition even approximating homogeneity. The crystals invariably were identical optically with the orthosilicate crystals, and in addition another compound was noted. This was a very fine grained material with a low refraction (less than 1.49) and an extremely low birefringence, and seems to be the modification of silica known as cristobolite. The evidence seems to be, therefore, that if the compound zinc metasilicate exists, it is unstable at its melting point. So it is certain, that notwithstanding the acidity of the fusions, the comparatively basic zinc orthosilicate crystallizes out. Perhaps the affinity of soda for twice and three times its molecular quantity of silica may further explain this phenomenon. J. W. Mellor,[7] investigating zinc crystalline glazes, succeeded in removing a crystal from adhering glaze and on analysis found:

	percent	CALCULATED FOR WILLEMITE *percent*
ZnO	68.83	68.83
SiO_2	27.15	25.36

Thus far, the compound separating from the melt has been zinc orthosilicate. In the region of

$$\left.\begin{matrix}10 \text{ percent } ZnO \\ 10 \text{ percent } Na_2O\end{matrix}\right\} 80 \text{ percent } SiO_2,$$

[5] *Zeit. Anorg. Chemie*, **69**, 142-7 (1910).
[6] *Sprechsaal*, **44**, 3 (1911).
[7] *Trans. Eng. Cer. Soc.*, **4**, 49 (1905).

the mat structure is due to a new type of crystallite. It is extremely small and without a definite crystal outline, even under the microscope. The birefringence is extremely low, the maximum interference color observed being a low order gray, and the index of refraction is slightly under 1.49. Hazy biaxial interference figures were obtained with difficulty, owing to the fineness of grain and low birefringence. In all determinable optical constants this compound is identical with cristobalite. No zinc orthosilicate crystals were found.

FIG. 4

FIG. 5

The glassy fusions were either colorless or of a slight greenish tint and offered little that was interesting megascopically. A microscopic study, however, was made of their refractive indices and of the influence of the zinc content on this highly important property. The method used was that of immersing fragments of the material whose index is sought in liquids of known indices. This method applied to glass fragments is accurate to about two in the third decimal place, and the accuracy is sufficient inasmuch as the individual fusions oftentimes showed variations of five in the second decimal place. Chemical inhomogeneity due to

segregation of the constituents is the prime factor affecting the refractive index. For comparison only the highest index was taken into account. Lorentz[8] and Lorenz[9] investigating the refractive index of substances, and its relation to the density, formulated independently of each other the following formula,

$$\frac{N^2-1}{N^2+2}\cdot\frac{1}{d}=K,$$

where N is the index of refraction of a substance; d, the density; and K, a constant for the substance independent of temperature and called the specific refractivity. For a solution,

$$K=\frac{P_1K_1}{100}+\frac{P_2K_2}{100}+\frac{P_3K_3}{100}+\ \ldots\ldots$$

where P_1, P_2 and P_3 are the percentages of the constituents and K_1, K_2 and K_3 their respective specific refractivities. Furthermore, Winkelmann and Schott[10] developed the following formula for computing the density of a glass from its constituents,

$$\frac{100}{D}=\frac{P_1}{d_1}+\frac{P_2}{d_2}+\frac{P_3}{d_3}+\ \ldots\ldots$$

where D is the density of the glass, d_1, d_2 and d_3 are the densities of the constitutents, and P_1, P_2 and P_3 their respective percentages.

Therefore, knowing the specific refractivities, densities and percentages of the constituents of the zinc, soda, silica glasses, it becomes a matter of computation to calculate the refractive index. The factors for soda and silica were the same as employed by Tillotson.[11]

They are as follows:

	SODA	SILICA
d	2.6	2.3
K	0.1302	0.1220

[8] *Wied. Ann.*, IX, 641 (1880).
[9] *Wied. Ann.*, II, 70 (1880).
[10] *Ann. d. Phys. und. Chem.*, 49, 401 (1893) and 51, 697 (1894).
[11] *J. Ind. Eng. Chem.*, 3, 897 (1911) and 4, 246 (1912).

The factors for zinc oxide were calculated from the density and average refractive index of willemite (73 percent. ZnO, 27 percent. SiO_2). The refractive index of willemite, 1.7063, and the density, 4.03, are the averages of values for these constants given in Dana's system. Applying the above formulae, the values for ZnO were computed as follows:

Density (d) 5.56
Specific refractivity (K)..... 0.09625

FIG. 6

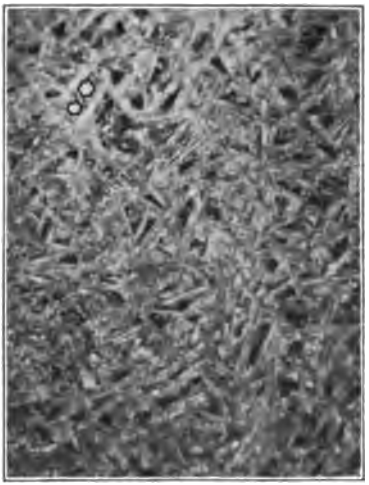


FIG. 7

The close agreement between the observed and calculated indices for six glassy fusions are given in Table I. The greatest variation noted was five in the third place, and this is remarkable considering the chemical inhomogeneity of the glass. However, the amount of lower refracting glass was often very small, especially in those glasses with a lower content of silica.

An interesting phenomenon was observed with glasses of comparatively high soda content, *e. g.*,

10 percent. ZnO
45 percent. Na_2O } 45 percent. SiO_2.

The microscopical examination of the fresh glass revealed absolute isotropy. With plane polarized light and crossed nicols the field was uniformly black. After the glass had weathered a few days, a zone of low birefringent material was formed around the edges of the glass grains. The new material was too minute for optical identification, but from the composition of the glass, it would seem to be a hydration product.

TABLE I

Showing the close agreement between the refractive indices of the glasses as observed and as calculated by the Lorenz-Lorentz formula.

COMPOSITION	OBSERVED	CALCULATED
.20 Na_2O, .25 ZnO } .55 SiO_2	1.569	1.570
.25 Na_2O, .20 ZnO } .55 SiO_2	1.551	1.552
.30 Na_2O, .15 ZnO } .55 SiO_2	1.548	1.545
.25 Na_2O, .10 ZnO } .65 SiO_2	1.528	1.525
.30 Na_2O, .20 ZnO } .50 SiO_2	1.561	1.560
.35 Na_2O, .10 ZnO } .55 SiO_2	1.537	1.536

SODA—ZINC OXIDE—TITANIC OXIDE—SILICA

Since most crystalline glazes of the zinc silicate type contain titanium, it was thought advisable to study the effect on soda-zinc oxide-silica fusions of the substitution of titanic oxide for a part of the silica. The amount of titanic oxide to be used was fixed arbitrarily at .2 molecule, replacing .2 molecule of silica in the original formulae. The above substitution was made in the

three series mentioned previously. Their formulae now became:

$$\left.\begin{matrix}.7\ ZnO \\ .3\ Na_2O\end{matrix}\right\{\begin{matrix}.2\ TiO_2 \\ \gamma\ SiO_2\end{matrix}\quad \left.\begin{matrix}.8\ ZnO \\ .2\ Na_2O\end{matrix}\right\}\begin{matrix}.2\ TiO_2 \\ \gamma\ SiO_2\end{matrix};\ \text{and}\quad \left.\begin{matrix}.9\ ZnO \\ .1\ Na_2O\end{matrix}\right\}\begin{matrix}.2\ TiO_2 \\ \gamma\ SiO_2\end{matrix}$$

The composition of the melts investigated, together with other data, is given in Table II. A comparison of these fusions with those containing no titanium oxide reveals a number of interesting facts. The presence of titanic oxide decreases the refractoriness of the melt. This is borne out by a comparison of a

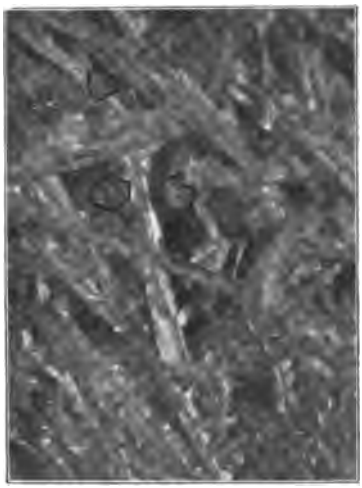


FIG. 8

FIG. 9

zinc-oxide-soda-titanic oxide-silica melt with the corresponding zinc-oxide-soda-silica one, *e. g.*,

$$\left.\begin{matrix}.8\ ZnO \\ .2\ Na_2O\end{matrix}\right\}\begin{matrix}2.1\ SiO_2 \\ .2\ TiO_2\end{matrix}$$

requires a temperature of 1300°, while

$$\left.\begin{matrix}.8\ ZnO \\ .2\ Na_2O\end{matrix}\right\}2.3\ SiO_2$$

requires a temperature above 1300°. This is but one of many comparison which demonstrate this fact. Finally, the presence

TABLE II

SODA—ZINC OXIDE—TITANIUM OXIDE—SILICA FUSIONS

COMPOSITION	TEMPERATURE OF BURNING	CHARACTER AND REMARKS
.3 Na_2O } .8 SiO_2 .7 ZnO } .2 TiO_2	1200°	Crystalline. Surface of melt appeared as one spherulite
.3 Na_2O } 1.3 SiO_2 .7 ZnO } .2 TiO_2	1200°	Crystalline. Crystals orientated irregularly. Some small spherulites.
.3 Na_2O } 1.5 SiO_2 .7 ZnO } .2 TiO_2	1200°	Crystalline. Individual crystals large.
.3 Na_2O } 1.7 SiO_2 .7 ZnO } .2 TiO_2	1200°	Crystalline. Individual crystals large.
.3 Na_2O } 1.9 SiO_2 .7 ZnO } .2 TiO_2	1200°	Crystalline. Individual crystals large.
.3 Na_2O } 2.1 SiO_2 .7 ZnO } .2 TiO_2	1200°	Crystalline. Individual crystals large.
.3 Na_2O } 2.3 SiO_2 .7 ZnO } .2 TiO_2	1300°	Crystalline. A few small spherulites in glass.
.3 Na_2O } 2.5 SiO_2 .7 ZnO } .2 TiO_2	1300°	Mat. Microscopically it consists of fine interlaced crystals.
.3 Na_2O } 2.7 SiO_2 .7 ZnO } .2 TiO_2	1350°	Mat. The interior of the melt has a bluish white stony appearance.
.2 Na_2O } .8 SiO_2 .8 ZnO } .2 TiO_2	1300°	Crystalline. Needle crystals well developed.
.2 Na_2O } 1.3 SiO_2 .8 ZnO } .2 TiO_2	1300°	Crystalline. Large radial spherulites.
.2 Na_2O } 1.9 SiO_2 .8 ZnO } .2 TiO_2	1300°	Crystalline. A number of smaller spherulites.
.2 Na_2O } 2.1 SiO_2 .8 ZnO } .2 TiO_2	1300°	Crystalline (?). Minute spherulites.
.2 Na_2O } 2.3 SiO_2 .8 ZnO } .2 TiO_2	1300°	Mat. It consists of minute crystals.
.2 Na_2O } 2.5 SiO_2 .8 ZnO } .2 TiO_2	1350°	Mat. It consists of minute crystals.

TABLE II—Continued

COMPOSITION	TEMPERATURE OF BURNING	CHARACTER AND REMARKS
.2 Na_2O } 2.7 SiO_2 .8 ZnO } .2 TiO_2	1350°	Mat. It consists of minute crystals.
.1 Na_2O } .8 SiO_2 .9 ZnO } .2 TiO_2	1300°	Crystalline. Large needles with porous matrix.
.1 Na_2O } 1.3 SiO_2 .9 ZnO } .2 TiO_2	1300°	Crystalline. Crystals are smaller than in preceding fusion.

of titanic oxide in a fusion raises the R O_2 content at which the crystalline, rather than the mat, structure persists. This is demonstrated by the fusion,

$$\left.\begin{matrix} .7\ ZnO \\ .3\ Na_2O \end{matrix}\right\} 2.3\ SiO_2$$

which possesses a typical mat structure, while

$$\left.\begin{matrix} .7\ ZnO \\ .3\ NaO_2 \end{matrix}\right\} \begin{matrix} 2.1\ SiO_2 \\ .2\ TiO_2 \end{matrix}$$

shows a large crystal growth. (See Fig. 5.)

The crystals of this series are of two types. The first is by far the most important. The crystals are long, prismatic, orientated irregularly, but more often as radial spherulites. (See Figs. 6, 7, 8 and 9.) In some of the spherulites, the crystals are so thin and acicular as to give rise to a sheaf-like structure. (See Figs. 10 and 11). Megascopically, the crystals are brownish yellow in color. Microscopically, the crystals are colorless and possess a hexagonal cross section. They show cleavage parallel to the *c* crystallographic axis and the extinction is parallel to the cleavage. The indices of refraction for sodium light are $\eta_e = 1.724 \pm .002$ and $\eta_o = 1.701 \pm .002$. The interference figures are uniaxial, and the optical character positive. The principal zone is also positive. The optical properties of this compound show a great similarity to those of the compound zinc orthosilicate, the only difference being a slight increase in refractive in-

dices and double refraction, which would be accounted for by the presence of a small amount of titanic oxide in the crystal. The evidence, therfore, shows that this compound is zinc orthosilicate containing a small amount of titanic oxide, and its formula may be written $2\,ZnO.SiO_2(TiO_2)$.

The second type of crystal is noted in the fusions of comparatively high titanic oxide content. Under the microscope, the crystals are minute prismatic in development and much intergrown. They are yellowish in color, but show no pleochroism. The refraction and double refraction are very high, probably

FIG. 10

FIG. 11

considerably higher than 2. Interference figures could not be obtained on account of the minuteness of the crystals and their intergrown character. From their high refraction, however, they must contain a large amount of titanium and are probably either titanium oxide or zinc titanate.

CONCLUSIONS

In melts of that part of the system, soda-zinc oxide-silica lying between the following concentration in molecular percentages: 90 percent. SiO_2, 10 percent. ZnO; 10 percent. ZnO, 50

percent. Na_2O, 40 percent. SiO_2; and 60 percent. ZnO, 40 percent SiO_2, three types of structures are encountered, glassy, mat, and crystalline. In the mat and crystalline melts, with one exception, the compound to separate out appears to be zinc orthosilicate. This closely resembles the mineral willemite in optical constants.

Allowing for the chemical inhomogeneity of the glass, the maximum indices follow the Lorentz-Lorenz law of specific refractivities fairly closely.

Glassy, mat and crystalline structures occur in melts of soda-zinc oxide-titanic oxide-silica composition. Two types of crystals are noted. One type is zinc orthosilicate containing a small amount of titanic oxide. The composition of the other type is unknown, but its peculiar optical properties point to either zinc titanate or titanium di-oxide.

QUESTION—CAUSES OF STONY GLASS AND THE RELATION OF POTASSIUM CARBONATE TO IT.

DISCUSSION CONTRIBUTED AFTER THE MEETING

Mr. C. J. Brockbank: In reply to the question, why does potassium carbonate cause stoning in glass, I would ask: Does it?

Potassium carbonate is an ingredient of all optical glass mixtures, and these glasses have to be absolutely free from stones. During more than seven years experience in the manufacture of optical glasses in Europe, the writer can only recall one instance in which K_2CO_3 was clearly responsible for stony glass.

We had been purchasing a crystallized pearl ash containing as high as 16 percent H_2O, and as long as the water was determined from time to time and the mixture corrected accordingly, we always got perfect results. This pearl ash was a by-product, and, when the firm making it changed their process, this source of supply was cut off. In its place, we purchased a pearl ash of a higher degree of purity, but perfectly dry, for which fact, we corrected the mixture. For some reason, that dry pearl ash would not dissolve in the glass, like the wet material, but floated to the top as scum or "salts." On the introduction of a wet proof rod to sample the glass, it would explode and splash some of this scum on the hood of the pot. Here, it would attack the clay and run back into the metal causing whitish stones, which would not dissolve in the metal. The usual remedy for salts was to throw a shovelful of wet cullet into the pot, but in this case, it was quite inoperative. Finally, we ceased using the dry material and the trouble disappeared. This would indicate that probably the physical state of the material may be important, apart from the chemical purity.

Some of the commoner stones and their causes are treated by me in another paper in this volume to which the reader is referred.

Mr. Frederic Carder: My observations and experience with closed pots, lead me to believe that the chief causes of stoning in glass, arise from the following:

1. Attack of materials on the pots.
2. Slow fusion.
3. Imperfect mixing of the batch.
4. "Silica grains," if they are too large in size.

1. The materials which go to make the batch, during the melting or nascent stage, attack the pots more and more after each melt; the bottom of the pots being usually more attacked than the sides. This goes on to such an extent that the pot becomes pitted and presents a honeycombed appearance. Parts of the pot so attacked usually present a whitish gray color and are very hard, giving the impression that the free silica and free alumina have been dissolved in the glass.

When the cold batch is thrown into the pot, these honeycombed portions become detached by being chilled and are disseminated throughout the glass during the melt. If the melting has not taken place under favorable conditions, these clay particles, will be found here and there suspended as it were in the glass as stones, mostly minute in size and can readily be detected, also the source from which they arise.

2. Slow Fusion. If the melting of the batch has been retarded, or the temperature not run high enough, stones will sometimes appear. but in a crystalline form. These look like silica grains suspended as it were in a glassy solution. Stones of this nature usually have a tear or striae trailing from them.

3. Imperfect Mixing of the Batch. In some batches, where the materials are weak in O or CO_2,stratification of the silicates is liable to occur, and the eagerness of the softer silicates in attacking the pots tend to produce stones.

4. If the silica grains used in the batch are too large in size, crystalline stones are liable to appear together with striae or cords. I have found that the only remedy in cases like this, is to

draglade or frit the mass and melt again, using a small proportion of the original batch with it.

The reason that K_2CO_3 causes stoning in glass, or as I should put it, why glass made with K_2CO_3 is more liable to stoning than glass made from Na_2CO_3 is, that the glass made from K_2CO_3 is not so liquid as that made from Na_2CO_3 or as the workmen say, it is stiffer and more easily gathered on the iron or pipe. This stiffness or more plastic nature retards the stones from coming to the top of the pot where they can be readily skimmed off. Many times when a pot used for K_2CO_3 glass becomes stony, and Na_2CO_3 glass is used afterwards, this pot will give good metal.

In support of this contention that a glass made from K_2CO_3 is more liable to stones, I have found, that when a pot is liable to form stones, if the glass is poled with a piece of wood when it is at its final melting stage, this poling causes a very violent reaction, making the glass boil, becoming more liquid and giving off large amounts of CO. If the pot is now run a few hours longer at the same temperature, the stones which were disseminated throughout the mass will appear on the surface and can be readily skimmed off. Care, of course, must be taken to counteract the reduction of the MnO_2 by a larger addition of this materal in the batch.

I believe that if glass could be treated somewhat similar to the Bessemer process for iron, that a lot of the troubles due to stoning would be eliminated.

There is not the least doubt, that if it were possible to use open pots instead of closed for lead glass, that the life of the pots would be materially increased, and the likelihood of stones decreased.

It must be apparent to you, that in a closed pot filled with a cold mixture, combination of the silicates take place nearest the source of the greatest heat or the pot wall; the heat being transmitted slowly through the mass to the center. It is during this period, that the side nearest the bottom is attacked so much.

On the other hand, if open pots could be used, the materials

commence to fuse at the top of the batch, and a more even distribution of heat is obtained through the mass.

It is possible that one or two of the causes I have enumerated may be present at the same time, as is often the case, and if the Ceramic Society want to confer a benefit upon the glass trade, I would suggest that it endeavor to give the potmaker a clay that will not be attacked so readily as those used at the present time.

EXPERIMENTS TO OVERCOME SCUMMING AND IMPROVE THE COLOR OF BRICK

BY A. E. WILLIAMS

The production of black and dark brown brick has come to be an important consideration to the face brick manufacturers. Many red-burning clays and shales are in use which will not withstand the severe reducing conditions and high temperatures necessary to produce these desired colors, or will not flash as easily as others because of differences in their physical and chemical composition. In the following work, experiments have been made in an attempt to develop an inexpensive method of producing these desired colors on such clays and shales.

The best method which suggested itself was to treat the surface of the column, as it issued from the die, with solutions containing salts of common metals.

Experiment I. Solutions used:

(a) Approximately 0.7 normal solution ferric chloride ($FeCl_3$) analyzing 113 grams Fe_2O_3 per liter.

(b) Approximately normal solution ferrous sulphate, using 300 grams $FeSO_4$ per liter and testing about 156 grams Fe_2O_3 per liter.

These solutions were sprayed on a column of clay as it issued from the die, using a clay which burned to a fair red color, but did not flash very dark at ordinary kiln temperatures.

Samples having both the smooth and rough or mat surface were cut from the treated column. Dry brick from two factories in Illinois were also sprayed with these solutions. These brick were all placed in a steam dryer for two days, and then burned in an open-fire down-draft test kiln. Samples were drawn from the kiln as follows:

1. Drawn at 1100° C., with kiln conditions oxidizing.

2. Drawn at 1150° C., two hours later, burning with gas conditions alternately oxidizing and reducing.

3. Drawn at 1200° C., two hours after drawing second trial and burning with gas conditions reducing.

The following shows the results obtained:

SAMPLES NOT TREATED	1ST SET	CLAY TREATED WET	CLAY TREATED DRY
Pale red. Signs of scumming.	$FeSO_4$	Pale red as clays not treated.	Pale red as clays not treated.
	$FeCl_3$	Darker red — no scum.	Pale red as clays not treated.
	2ND SET		
All scummed and have dirty gray color. Flashing not effective.	$FeSO_4$	Grayish brown; better than sample; not treated.	Same as sample, not treated.
	$FeCl_3$	Chocolate brown, good color.	Same as sample, not treated.
	3RD SET		
Flashed shiny black.	$FeSO_4$	Flashed shiny black.	Flashed shiny black.
	$FeCl_3$	Flashed shiny black.	Flashed shiny black.

The above results lead to the following conclusions:

1. Treating dried brick with ferrous sulphate or ferric chloride gave no satisfactory results.

2. Treating the clay column while still wet, showed an improvement in the color, principally by giving a surface free from whitewash.

3 Ferric chloride was much more effective than the ferrous sulphate.

4. A slight amount of flashing gave brick a darker color when treated with $FeCl_3$.

Experiment II. As a continuation of these experiments, another set of samples was made using the same clay which was treated in the stiff-mud condition in the first experiment and two

other clays which were known to scum and give a generally poor color when not treated with barium compounds.

Five sets of trials were made from each clay, as follows:

1. Rough and smooth faces not treated.

2. Rough and smooth faces treated with ferrous sulphate.

3. Rough and smooth faces treated with ferrous sulphate, then with ammonia to precipitate ferric hydroxide.

4. Rough and smooth faces treated with ferric chloride.

5. Rough and smooth faces treated with ferric chloride, then with ammonia as in set No. 3.

These bricketts were placed in saggers, covered well to prevent any flashing effect of the open fire, and burned to 1150° C. in 36 hours. The results are shown in Table I.

TABLE I

Set No. 1	Set No. 2	Set No. 3	Set No. 4	Set No. 5
Rough and smooth faced samples showed scummed surfaces with grayish color.	Rough faced samples appeared considerably better than untreated samples but did not give a clean red color. Smooth face samples not much improved.	Same as No. 2.	Rough faced samples showed good clean bright red. Smooth faced samples greatly improved.	Rough and smooth faced samples showed good clean red color, except where there was slight flashing.

This experiment confirmed the conclusion from experiment 1, that ferric chloride was actually overcoming the effects of scumming.

Experiment III. The effect of volatilizing ferric chloride in a kiln was also tried. The test kiln was set with half-brick and burnt to 1000° C. in 48 hours. One-half pound of ferric

chloride was then put in each of the two fire boxes, the damper closed until the fumes were coming very slightly out of the fire boxes, and the kiln kept in that condition for one-half hour. The kiln was then fired in the regular manner, and samples drawn one-half hour later. This treatment seemed to have had no appreciable effect on the color.

The temperature of the kiln was then raised to 1100° C., and ferric chloride used in the same manner as before, but with the same results.

Finally, the kiln was finished at 1150° C., at which time a third treatment of ferric chloride was given, after which, firing was discontinued, and the kiln cooled in the regular way. When the kiln was opened everything was flashed to a dark brown color, but whether or not the high temperature and somewhat reducing condition was as much the cause of the color as the ferric chloride is an unsettled question.

The results at this time indicated that ferric chloride was assisting the flashing somewhat, but more especially was producing good clean red colors, free from scumming. Comparing the cost of ferric chloride with the cost of barium compounds and also the relative quantities used, the cost of using ferric chloride would be considerably cheaper, costing about two cents per thousand brick. The balance of the experimental work was therefore done on a commercial scale at three different factories where a considerable amount of barium is now being used. The results in detail are given below.

The method of spraying the column of brick on a commercial scale was tried, but gave considerable trouble, and the simple but effective method of using a roller 3 inches or 4 inches in diameter and covered with lamb's wool, placed in front of the die was adopted. The ferric chloride solution was allowed to drop from glass stop-cocks onto the roller.

At one factory, about six thousand brick were made with a solution of one-half pound commercial ferric chloride per gallon of water, which was applied to the column at the rate of one gallon per six thousand brick.

At another factory, three trials were made, using one, one and a half, and two pounds of commercial ferric chloride per gallon of water and spreading the solution on at the rate of one gallon per three thousand brick. All of these trials resulted in a failure so far as removing the scum was concerned, although the last trial using two pounds per gallon of solution produced an appearance on the brick similar to that found when barium compounds had been added in an amount not quite sufficient to completely remove all of the scum, forming a rather pimpled effect with the under color good. It is intended that further practical tests of this sort will be made in an effort to overcome scumming.

The reason for the effects of ferric chloride in reducing the scumming are not as yet clear. $Fe_2Cl_6.6\,H_2O$, either alone or mixed with powdered gypsum gives up a large quantity of HCl below 200° C., and the last traces are driven off below 250° C. There is no evidence of SO_2 being present in the gases expelled from the mixture of ferric chloride and gypsum, and therefore no indication of the decomposition of the sulphate.

The fact that the trials treated with ferric chloride and ammonia showed as good a color as the trials treated with ferric chloride alone would lead one to believe that the improvement is not due to the free HCl evolved.

It is shown by H. O. Hofman and W. Mostowitsch[1] that the presence of SiO_2 or Fe_2O_3 lowers the dissociation temperature of $CaSO_4$. In heating with SiO_2, decomposition was first indicated by the evolution of SO_2 at 1000°C.; with Fe_2O_3, dissociation of the sulphate was first indicated by the evolution of both SO_2 and O at 1100° C.

This may explain why such results are obtained in a test kiln, using temperatures above 1100° C., and not in a commercial kiln using temperatures between 1000° and 1050° C. The sulphates coming to the surface in the process of drying brick would, no doubt, become more or less mixed with the ferric oxide present, and this condition would compare favorably with the

[1] The Behavior of Calcium Sulphate at Elevated Temperatures with Some Fluxes. *Transactions Inst. of Mining Eng.*, Vol. 39, page 628.

experiments of Hofman and Mostowitsch. On the other hand, the entire effect may be simply one of covering the scumming.

Further experiments in producing dark colors were made in commercial kilns by the introduction of manganese chloride, and copper chloride into the kiln at the completion of the burn.

The burns, in which these salts were introduced, were carried on under oxidizing conditions, and the resulting colors would ordinarily have been light chocolate on the brick in the top 10 courses and a red color in the lower part of the kiln. At the finish of a burn after the fires had become free from flame, twenty-five pounds of manganese chloride was put into the top hole of the kiln crown, and the damper of the kiln nearly closed. There was evidence of fumes going through the kiln over a period of about five minutes. The damper was left closed for one-half hour, however, and the kiln finished in the regular manner. The brick in this kiln were well blackened, in the form of an inverted cone from the top about half way down. In all probability, if this kiln had been flashed for black brick an even larger number would have shown the effects of the manganese. However, this gives a method of blackening ware without flashing it to a very great extent and risking the results of overburned brick.

The price of manganese chloride at the time these experiments were made was about six cents per pound, but since then it has been advanced very considerably in price

Treating a kiln with copper chloride in the same manner as above gave no marked effect. If anything, only a slight tendency to give a brown color might be attributed to it.

The volatilization of ferric chloride in commercial kilns has not yet been tried. It is possible, that this salt will assist in giving a black color.

Summary. 1. Treating the surface of a stiff-mud clay column with ferrous sulphate did not markedly effect the color in burning.

2. Treating the surface of a stiff-mud clay column with ferric chloride did improve the color, evidently by removing the scumming, but as yet no good results in commercial kilns have been obtained.

3. Manganese chloride, volatilized in brick kilns at the finish of a burn, produced dull black colors with but little previous flashing of the kiln.

4. Coper chloride gave very little evidence of darkening the color of the brick.

In conclusion the writer desires to acknowledge his indebtedness to his co-workers of the Department of Ceramic Engineering, University of Illinois.

A MODERN DRY-PRESS AND STIFF-MUD BRICK PLANT.

BY T. W. GARVE

The following is a brief description of a combined dry-press and stiff-mud brick plant which has recently been completed and is now in successful operation in North Dakota. The description of the dryers and kilns will not be taken up but merely the machinery layout and manufacture of the ware which is fire brick and face brick.

The problem was to grind and properly prepare the clays, to mix them, to steam the dry-press clay, to provide for storage as well as for immediate use of the prepared material, one kind as well as mixed.

In Fig. 1, we have a layout of the factory with the following group of buildings:

The clay trestle (with storage for raw clay along one side).

The clay preparing building.

The clay storage building.

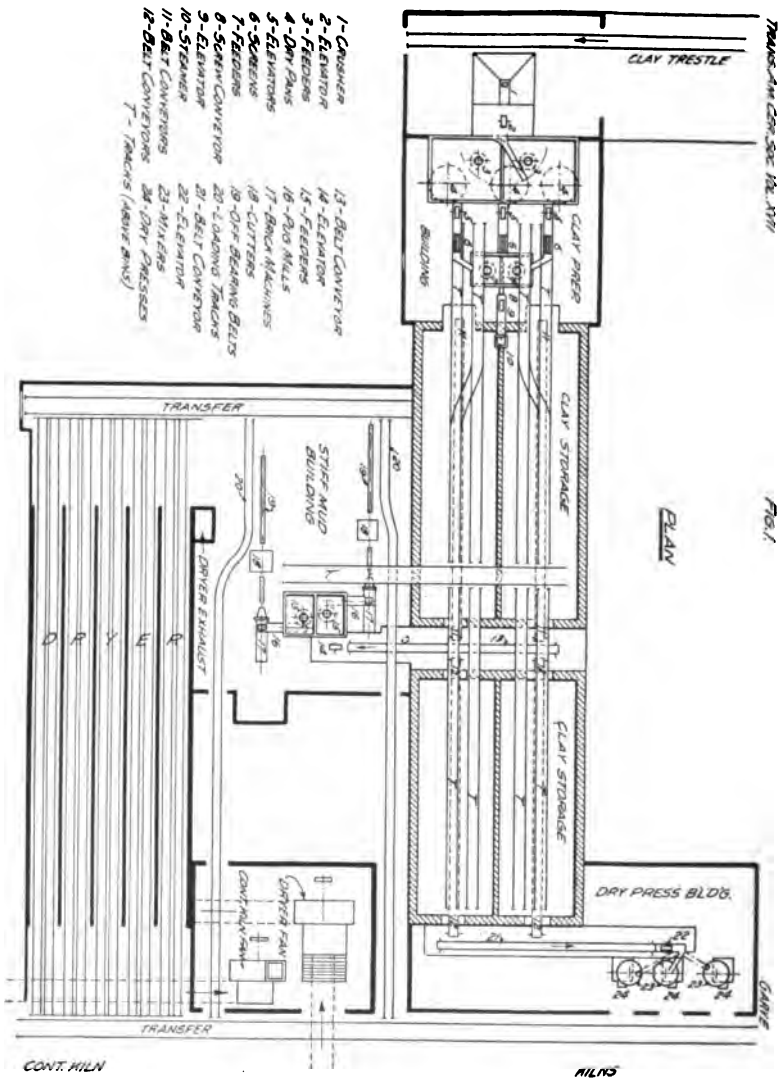
The stiff-mud brick building (with dryer).

The dry-press brick building.

Machinery. In the clay preparing building, we have one jaw crusher, one elevator, two clay storage bins with two feeders, three dry pans, three elevators with three screens, two clay bins with two feeders, one screw conveyor, one elevator, and one steamer.

The clay storage building consists of two large bins for the stiff-mud clay and two somewhat smaller bins for the dry press clay. There are tracks (T) above the bins, one belt conveyor under each bin, one cross conveyor for the stiff mud delivery (13), and one cross conveyor for the dry press delivery (22).

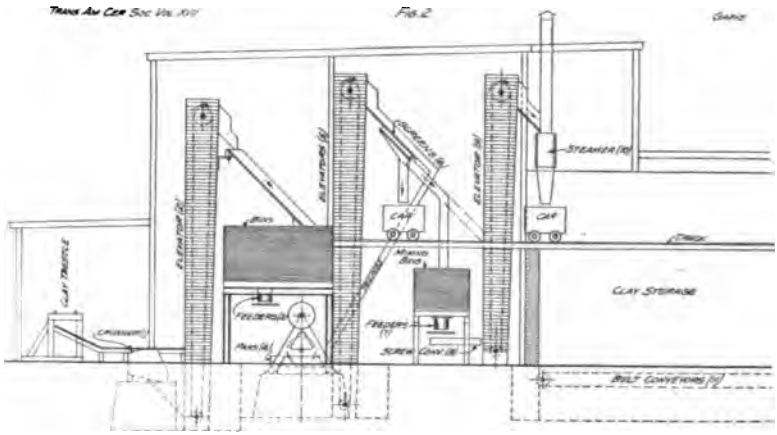
In the stiff-mud brick building, we have one elevator, two clay storage bins with two feeders, and two lines of machinery consisting of pug mill, auger brick machine, cutter, and off-bearing belt.


1-CRUSHER
2-ELEVATOR
3-FEEDERS
4-DRY PANS
5-ELEVATORS
6-SCREENS
7-FEEDERS
8-SCREW CONVEYOR
9-ELEVATOR
10-STEAMER
11-BELT CONVEYORS
12-BELT CONVEYORS
13-BELT CONVEYOR
14-ELEVATOR
15-FEEDERS
16-PUG MILLS
17-BRICK MACHINES
18-CUTTERS
19-OFF BEARING BELTS
20-LOADING TRACKS
21-BELT CONVEYOR
22-ELEVATOR
23-MIXERS
24-DRY PRESSES
T-TRACKS (ABOVE BINS)
CLAY TRESTLE
CLAY PREP
BUILDING
CLAY STORAGE
CLAY STORAGE
STIFF MUD BUILDING
TRANSFER
TRANSFER
DRYER EXHAUST
DRYER
DRYER FAN
CONT. KILN FAN
DRY PRESS BLDG.
PLAN
FIG. 1.
CONT. KILN
KILNS
GARVE

In the dry-press brick building, we have one elevator, three mixers, and three presses.

Processes. With this layout, we are getting the following manipulations or processes (See Fig. 3):

1. Raw clay over clay preparing machinery to bins, one kind or mixture.
2. From bins to stiff-mud plant or dry-press plant.
3. Direct from clay preparing machinery to stiff-mud plant or dry-press plant (if desired).



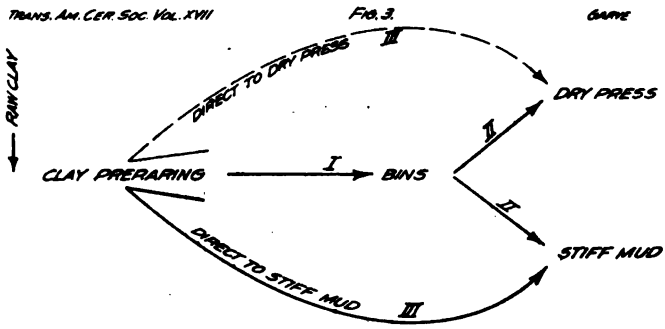
CLAY PREPARING BUILDING
ELEVATION

1. Raw clay over clay preparing machinery to bins, (see especially Fig. 2). The raw clay is hauled up the incline and dumped in front of a jaw crusher. Here, the material is crushed, then elevated and fed into overhead storage bins, from which it is drawn out, at the bottom by disc feeders which drop the material into pans. Here the clay is finely ground, then elevated and screened.

Where a single clay is required, the screen chute feeds two cars, alternating one at each side of the screen. The cars are run to the clay storage building, and the clay dumped into its proper bin.

For making a mixture, the screened materials chute into small bins from which they are drawn out by disc feeders, which measure the relative required quantity of each. A screw conveyor between the two feeders mixes the materials and feeds an elevator, which carries the materials up to the steamer; and from the steamer, the clays drop into cars for dry press brick, or direct from elevator into cars for the stiff-mud brick. These cars are on the same tracks as described previously, so they are taken to storage in the same fashion.

2. From bins to stiff-mud plant or dry-press plant. For using stored clay for the stiff-mud plant, we take the clay from storage by one or two underground belt conveyors (11) which



feed a cross belt conveyor (13), and this in turn carries the clay to an elevator (14), where it is elevated and delivered into bins. From the bottom of these bins, the clay is drawn out by disc feeders, one for each line of machinery consisting of a pug mill, auger brick machine, cutter and off-bearing belt.

Close to the off-bearing belts are the loading tracks, marked 20 on Fig. 1.

The ware then passes through the tunnel dryer to a continuous kiln.

The clay from the dry-press-storage building can be used for stiff-mud manufacture by running the underground conveyors (12) towards the cross conveyor (13). The necessary driving mechanism has been provided for.

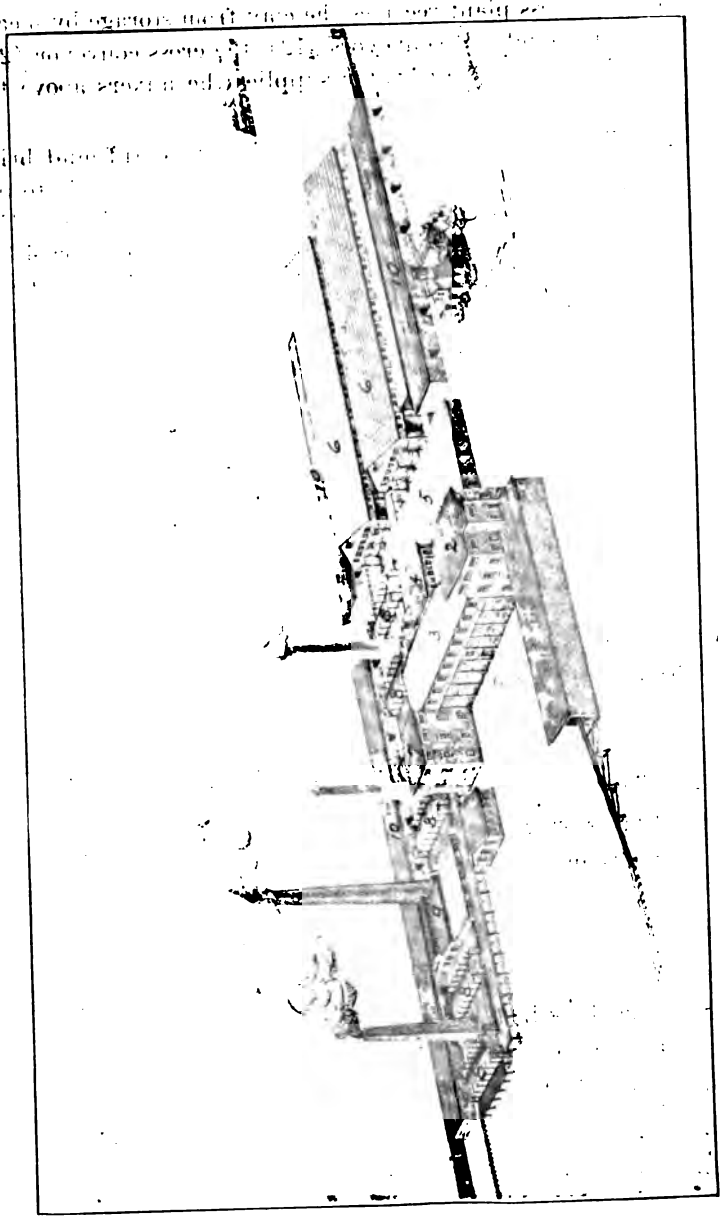


FIG. 4

The dry-press plant receives the clay from storage by means of the underground belt conveyors (12), the cross conveyor (21) and elevator (22). The elevator supplies the mixers above the presses.

3. Direct from clay preparing building to stiff-mud brick plant or dry-press brick plant. Provision has been made to use the prepared material direct for the manufacture of brick. For this purpose, the cars from the corresponding elevators for either kind of clay or a mixture are moved over to the stiff-mud brick building by means of a special transfer track. The clay is then dumped into the small bins above the feeders (15).

The clay or clays for the manufacture of dry-pressed brick are obtained and stored as described. Here, we are enabled also to use the materials direct by dumping the clay from cars into the mixers or small auxiliary bins above. As a rule, however, the steamed material is stored and allowed to sweat.

If the dry-press plant requires only one kind of clay, the mixing outfit (6, 7, 8) might be omitted, and the clay from the screens (6) chuted over direct into the elevator (9) for steaming and then to cars as before.

Figure 4 gives a birdseye view of the complete plant. There are:

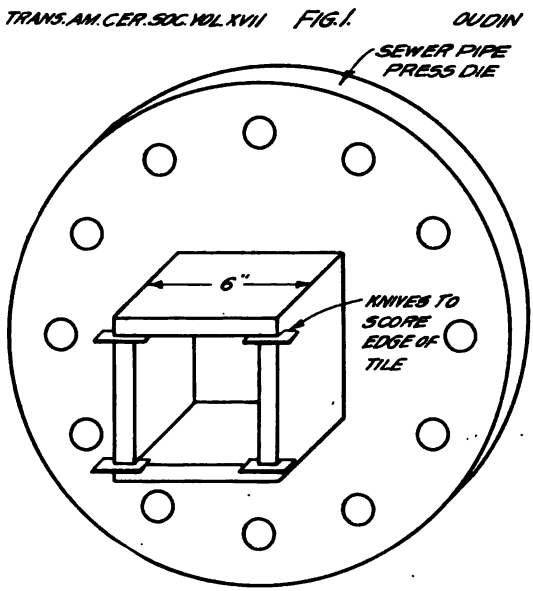
1. Raw clay storage building.
2. Clay preparing building.
3. Clay storage building.
4. Stiff-mud brick building.
5. Dryer.
6. Continuous kilns.
7. Dry press brick building.
8. Periodic kilns.
9. Power house.
10. Stock sheds.

QUARRY TILE.

BY C. P. OUDIN, SPOKANE, WASH.

To produce an old thing a new way may be of interest to my fellow clay-craft workers.

To manufacture 4 by 6 inch and 6 by 6 inch quarry tile without the necessity of repressing, and without the difficulties of drying and setting each tile indepedently was the problem, the solution of which was found in the process herein given.



We all know the troubles which the brick machine gives us and the laminations found in the column of clay that they produce. With the sedimentary clays of Washington, our troubles from these sources are especially severe. "Necessity is the Mother of Invention," and in our search, we tested out the steam sewer-pipe press and in it. found the solution of the problem.

The equipment which we finally adopted is as follows: One 9 ft. dry pan, two 8 ft. wet pans, rapid feeder for the press, and one single rod sewer pipe press, all Stevenson machinery.

To the pipe press, we fasten our new die for the making of quarry tile, a sketch of which is shown in Figure 1.

The quarry tile is made with saw steel linings, so as to standardize the size of the tile. At each corner, a steel marker scores the tile, so that when burnt they break at the corners, where scored, making the two 6 in. by 6 in. and the two 4 in. by 6 in. tile. Fastened to the core or center of the die, are four small round wheels making the initials of the manufacturer on the

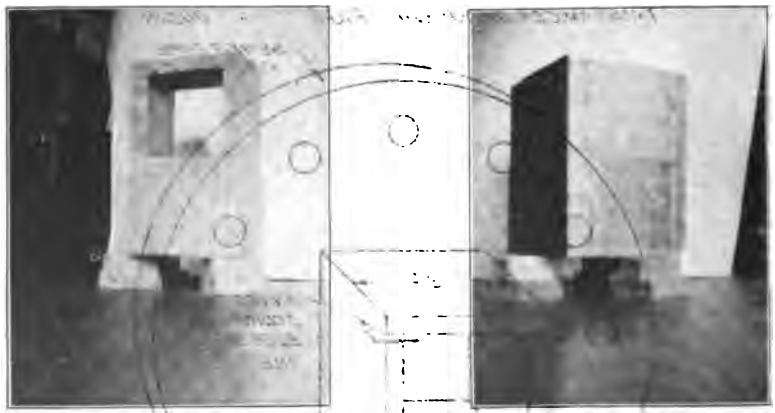


FIG. 2a FIG. 2b

under side of each tile. The clay is forced through this die onto a chinaman cutter making two 6 in. by 6 in. and the two 4 in. by 6 in. tile at one time.

These are carried on end on palletts to the drying floor. While on the drying floor, the edges of the tile are sponged to take off any rough edges that might be left in scoring and to insure all perfect goods. When dry, these square tubes are taken to a kiln. The setting and glazing is the same as for sewer pipe.

Figures 2a and 2b are illustrations of the burnt and glazed tile.

GALENA AND LEAD-BEARING WASTE MATERIALS AS GLAZE INGREDIENTS[1]

BY JULIUS MILLER

This paper records the results of an investigation as to the adaptability of cheap lead glazes to common ware, the glazes containing galena as the source of the lead. Since there are other lead bearing materials cheaper than galena, it was decided to include these also, and the investigation covered the four types of lead bearing materials, *viz.*,

Galena.
Lead sulphates.
Lead peroxides.
Dusts (flue dusts and baghouse dusts).

The study in outline covered the following:

A. Investigation as to resource, quantity and cost of galena and waste lead-bearing materials and the obtaining of samples from the various plants.

B. Chemical analysis of samples for Pb content. Preliminary fusion tests.

C. Preparation of tile bodies using the following clays to represent the common ware industries:

No. B =Bedford shale from Ohio.
No. 128=Beaver Valley shale from Pennsylvania.
No. 157=Zanesville stoneware clay, a No. 2 fireclay from Ohio.

The determination of maturing heats of above bodies to form hard semi-vitrified bodies.

D. The obtaining of cheap standard glazes for each of the above-named bodies, at their respective maturing heats.

The following ingredients to be used:

Litharge (PbO).
Whiting.
Clay (Eng. china).
Flint.

[1] Thesis, Ohio State University, 1915.

E. The substitution of the lead samples for the litharge in the standard glazes obtained, according to Pb content of samples.

The following operations are included under this heading:

1. Compounding of glazes using the waste-lead and galena samples as the lead-bearing ingredients.
2. Spraying of glazes on tile.
3. Determination of weight of the amount of dry glaze sprayed on each tile.
4. The burning of glazed tile at their respective heats.
5. The study of each series of burned tile and glazes.

F. Conclusions derived from results obtained in this investigation.

Letters inquiring as to the kind, amount, price and asking for samples, were sent to all known active lead smelters, refineries and mines of this country. Twenty-six companies answered, of which number fifteen encouraged this investigation. Nine of the fifteen sent samples as directed. Enough samples were sent to represent the four kinds of materials chosen, and are as follows:

Galena—sample No. 1.
sample No. 3.
Lead sulphate—sample No. 4.
Lead peroxide—sample No. 6.
Dusts—sample No. 7 (flue dust).
sample No. 12 (baghouse dust).
sample No. 14 (baghouse dust).
sample No. 20 (blue fume, a baghouse product).

Over half the number of lead companies in the United States have waste lead-bearing materials in the form of dusts, sulphates, peroxides, oxides (skims), slags, mattes and galena concentrates, which they are willing to market from 1½ cents to 3¼ cents per pound, *f. o. b.* their plants. The Pb content of these materials varies from 10 to 85 percent.

Two preliminary fusion tests were run in order to determine the relative fusibility, burning properties and physical properties of the samples. The samples having the highest Pb contents

and least amounts of foreign impurities fused earliest, and gave smooth, glossy, and colorless glaze. Samples containing impurities were colored according to the amount and kind of impurity present.

Since the galena, sulphates, peroxides and flue dust were of a coarse-grained nature, they were subjected to a grinding test. This test showed that it was impractical to grind such material dry in the ball-mill as they have a tendency to coat and clog the balls and the inside of the ball mill, after being ground to a certain fineness. Wet grinding would not only be a very practical way of grinding, but gives a more uniformly mixed, and a finer ground material.

All samples were analyzed for Pb content, according to Wilder.[1] Check analyses and additional analyses of sample No. 7 for SiO_2, Al_2O_3 and Fe_2O_3 were run. Results:

SAMPLE NO.	LEAD	
	percent	
1	83.5	
3	82.5	
4	52.5	
6	73.0	
7	41.5	4.3 SiO_2 · 13.3 Al_2O_3 · 3.2 Fe_2O_3
12	42.3	
14	71.3	
20	78.8	

In order to represent the clay bodies of the common ware industries, the clays were crushed, ground wet, tempered and forced through a tile die. All tile were cut in uniform lengths. In a series of burns, the bodies were found to mature to the desired vitrification at the following cones:

Body No. B at cone 02
Body No. 128 at cone 2
Body No. 157 at cone 6

These maturing heats represent the range of maturity of all common ware industries, and therefore are suitable for this

[1] Lord and Demorest, *Metallurgical Analysis*, p. 209.

study. The shales are red-burning, subject to flashing, while the fireclay is buff-burning, subject to blue-stoning.

In order to study the analyzed samples as glaze ingredients, the following method of investigation was carried on:

A standard glaze for the maturing temperature of each body was obtained, using litharge (PbO), whiting, English china clay and flint as the standard ingredients. Having obtained a good commercial glaze for each body, and knowing the percent Pb content of samples by analysis, these samples were substituted for the litharge in the glazes, the substitution being based on the Pb content of glaze.

The standard glazes were obtained according to following practice:

All glazes were determined by choosing two end members, which have a constant Al_2O_3 and SiO_2 content. One end member has the maximum PbO and minimum CaO contents, while the other end member the minimum PbO and maximum CaO contents. These end members are blended to form a series of members, such that the PbO and CaO content will vary uniformly throughout the series. Each member of series was sprayed on the tile bodies, and burned to the correct maturing temperature. The best glaze of the series, and this must be a smooth bright surface, free from faults, was then chosen as the standard glaze for the body used.

Standard Glaze for Cone 02 (Body No. B). From experience, it was found that a ratio of 1 Al_2O_3 to 10 SiO_2 gave the best results in the raw lead glaze studies at cone 02. The following end members were then chosen for this cone:

$$\text{Mem. (A)} \quad \left.\begin{matrix} .7\ PbO \\ .3\ CaO \end{matrix}\right\} .15\ Al_2O_3 : 1.5\ SiO_2$$

$$\text{Mem. (B)} \quad \left.\begin{matrix} .3\ PbO \\ .7\ CaO \end{matrix}\right\} .15\ Al_2O_3 : 1.5\ SiO_2$$

The glaze of this series chosen as the standard glaze is:

$$\left.\begin{matrix} .55\ PbO \\ .45\ CaO \end{matrix}\right\} .15\ Al_2O_3 : 1.5\ SiO_2$$

Standard Glaze for Cone 2 (Body No. 128). In the cone 02 series, it was found that as the CaO content increased, the glazes appeared scum-like and whitened, indicating immaturity. The same series, therefore, were tried again at this cone. An additional series, similar to cone 02 series, but with an increase of clay and flint to .2 Al_2O_3 and 2.0 SiO_2, respectively, were made up and tried.

The results of this burn gave the following as the standard glaze for cone 2:

$$\left.\begin{matrix}.3\ PbO \\ .7\ CaO\end{matrix}\right\} .15\ Al_2O_3 : 1.5\ SiO_2$$

Standard Glaze for Cone 6 (Body No. 157). In the cone 2 series, it was found that an increase of clay and flint tended toward opacity or a raising of the maturing temperature of glaze; therefore the same series were tried at this cone.

The results of this burn gave the following as the standard glaze for cone 6:

$$\left.\begin{matrix}.3\ PbO \\ .7\ CaO\end{matrix}\right\} .15\ Al_2O_3 : 1.5\ SiO_2$$

In the selection of these glazes, the uniformity of heat treatment was taken into consideration. It was found that a spray of 30 pounds per 1,000 square feet, using the standard glaze of cone 02, and a spray of 25 pounds per 1,000 square feet of surface, using standard glaze at cones 2 and 6, gave the best results.

It is to be understood that, in this investigation, the mode of application of all glazes to the tile bodies was by the use of a spraying apparatus.

Having obtained standard glazes for cone 02, and cones 2 and 6, the amount of the analyzed samples to be substituted in these glazes for the litharge was determined in the following manner:

Let x equal amount of litharge in grams, used in a 200 gram batch of glaze.

Litharge contains 92.82 percent of Pb.

Let y equal percent of Pb in one of the analyzed samples.

Therefore we would use:

$$\frac{92.82}{y}\ (x) \text{ or } ``n'' \text{ grams of the sample.}$$

The glaze numbers in Tables I and II are the same as the sample numbers.

TABLE I—BATCH WEIGHT OF GLAZE IN GRAMS FOR CONE 02

Glaze No. ...	1	3	4	6	7	12	14	20
Sample	95.4	96.6	152.0	109.2	192.0	188.4	111.8	101.0
Whiting	31.5	31.5	31.5	31.5	31.5	31.5	31.5	31.5
Clay	27.1	27.1	27.1	27.1	27.1	27.1	27.1	27.1
Flint	50.4	50.4	50.4	50.4	50.4	50.4	50.4	50.4

TABLE II—BATCH WEIGHTS OF GLAZE IN GRAMS FOR CONES 2 AND 6

Glaze No. ...	1	3	4	6	7	12	14	20
Sample	119.0	120.4	189.2	136.1	239.4	234.8	Sample gone	125.9
Whiting	112.0	112.0	112.0	112.0	112.0	112.0		112.0
Clay	61.9	61.9	61.9	61.9	38.0	61.9		61.9
Flint	115.2	115.2	115.2	115.2	153.0	115.2		115.2

These batches were ground wet in ball mills for four hours. They were then brought up to proper consistency for spraying and sprayed on their respective bodies. In order to determine the proper amount of glaze to be used for best results, each glaze was sprayed on three tile, a light, medium and a heavy spray. The weight of the amount of glaze sprayed on each tile was obtained by weighing bone dry tile before spraying, and weighing sprayed tile after drying. The difference in weights is the weight of dry glaze on the tile.

Two burns were made at cone 02. The first burn was made in a direct gas-fired, updraft kiln, and glazes and tile showed the effect of a very non-uniform firing. A second series was then burned in a muffle kiln with a liberal access of air to ware at all times of burn. A good uniform heat treatment was obtained in this way.

It was also found necessary to make two burns for the cone 2 study. In order to protect the tile from direct flame, since the same direct gas-fired kiln was used, the tile were placed in saggers. The first burn showed the effect of two different heat zones existing in the kiln, and therefore a fair study of tile could not be had. Advantage was taken of this fact, and kiln was set to correct this fault, with good results.

Two burns were made at cone 6, but the results showed that the limit of the maturing range for good raw lead glazes had been exceeded. The same direct gas-fired updraft kiln was used in this study.

CONCLUSIONS DERIVED FROM RESULTS OBTAINED IN THIS INVESTIGATION

Galena. Sample No. 1 is a concentrate as obtained from the concentrating tables and sample No. 3 is a pure mineral. If galena is to be used at all, it must be introduced in the very pure form of which these two types are the most economical to use. The presence of impurities such as Fe_2O_3, ZnO, etc., tend to color and opacify the glaze.

As a glaze ingredient, galena introduces a considerable amount of sulphur, which must be burned off slowly in an oxidizing atmosphere. The presence of this impurity will make the time of burn longer. This fact was proven by the whiteness or colored opacity which was found to prevail to a more or less extent in the cone 02 and 2 studies, this being the only fault of glaze. It was found by microscopic investigation, that this whiteness or opacity was due to immaturity. On first examination with a magnifying glass, I thought that this whiteness was due to numerous bubbles of entrapped air, but on further microscopic investiagtion, undissolved $CaCO_3$ was detected as being the real cause. The vesicles, however, aid in causing this fault. This investigation showed that conditions of saturation either made it impossible for all material to go into solution, or that heat treatment had not been sufficient at that stage. The first is not likely, since the standard glazes showed that all material had gone into solution during the same heat treatment. The lat-

ter explanation is the more probable, since the presence of sulphur and other impurities requires additional heat to burn them out, such as the using up of heat required to decompose the $CaCO_3$ ($800°C$). As a result, when this fact is not taken into consideration, and the burn finished as when using litharge, an immature, whitened and vesicular glaze is obtained. The presence of the undissolved $CaCO_3$ indicates that the vesicles are in part formed by CO_2 (decomposition of $CaCO_3$) and SO_2 or SO_3 from the impurities, and, with a longer heat treatment at this stage, the reactions of decomposition and oxidation would go to completion, and by a gradual rise to finishing temperature, the glaze would clear up. The foregoing explanation is further strengthened, in that the whiteness increases with increase of glaze on the tile; and also in that it seemed to prevail in the high lime end of the standard glaze series at the respective heat treatments.

Good glazed surfaces are produced on the Bedford and Beaver Valley shales, the only fault being the above mentioned opacity or whiteness. The maturing ranges of these shales lie between cone 03 and cone 3.

The cost per pound of galena is 3¼ cents. The galena glaze for cone 02 was calculated to cost $12.00 per ton less than standard glaze using litharge. For cone 2, the galena glazes were calculated to cost $7.50 per ton less than standard glaze. At cone 6, the glazes were badly blistered due to over-firing.

The light sprays of both samples were found to give the best results in each case and are as follows:

At cone 02 on No. B body—52 pounds per 1,000 square feet of tile surface.

At cone 2 on No. 128 body—25 pounds per 1,000 square feet of tile surface.

Another point in favor of the use of galena is that it is an insoluble compound, and therefore, danger of lead poisoning is greatly lessened.

Lead Sulphate. Sample No. 4. This waste lead material can only be used economically when obtained in the dry calcined

form. When grinding dry in ball mills, the same trouble of clogging and packing about the balls and the mill was experienced, but to a lesser degree than in the use of galena. The wet grinding process would be the most economical one to use.

As a glaze ingredient at cone 02, better results than those in the use of galena were obtained. The opacity (slightly tinted by Fe_2O_3) was present to a much lesser degree than in use of galena, and is due to same cause, since this material introduces sulphur in the sulphate form. It is therefore evident that the same caution as to firing must be taken, as when using galena. At cone 2, very good glazes were produced on body No. 128, and they are as good as standard glazes, being almost entirely free from opacity, due to the longer and better heat treatment obtained in this burn. At cone 6, the glazes were badly blistered due to overfiring.

It is evident that this material can be used successfully as a glaze ingredient in glazes maturing from cone 02 to cone 2 on shale and fireclay bodies, provided firing is carefully done, and the glazes are protected from direct flames.

The cost per pound of this material was quoted at 2½ cents. At cone 02, the glaze using lead sulphate was calculated to cost $33.00 per ton or $14.48 less than cost of standard glaze using litharge. At cone 2, the cost is $26.00 per ton of glaze or $6.92 per ton cheaper than standard glaze.

The light sprays gave the best results, and are as follows:

At cone 02 on body No. B—61 pounds per 1,000 square feet of tile surface.

At cone 2 on body No. 128—48 pounds per 1,000 square feet of tile surface.

Lead Peroxide. Sample No. 6. This material was a failure when used as a glaze ingredient in the type of glaze employed in this investigation. However, the fusion tests show that this material is a good flux.

Dusts. The dusts as a whole gave the best results in this investigation. The baghouse dusts are exceedingly fine grained, light, black and oily and can be used directly from the plant

without any preliminary grinding. The flue dust is coarse grained and light brown in color and must be ground. The same trouble of clogging and packing of this material in ball mills was experienced, and this dust would therefore have to be ground wet.

In the fusion tests, the baghouse dusts produced good results when used in large amounts, since the material is of low density. The flue dust produced a coffee-colored mat glaze when used by itself. The baghouse dusts showed bright surfaces at cone 04, while the flue dust brightened at cone 03.

Flue Dust. Sample No. 7. According to qualitative tests, As, Sb, Zn and Fe were found to be present in addition to the 41.5 percent of Pb in the sample. As a glaze ingredient, it introduces very little sulphur or carbon, and therefore good glazes were produced in burns of the same length as in standard glazes. Due to the presence of impurities, (As, Sb, Zn and Fe), a different type than that of standard glaze was produced at each cone. At cone 02 on No. B body, this flue dust glaze produced the smoothest and brightest surface of the study, free of vesicles, and of an opaque deep red color, the red color being possibly due to the oxysulphide of antimony. At cone 2 on body No. 128, a bright, smooth, opaque, yellow glaze was produced. The opacity was sufficient to mask the red-burning body. The yellow color is possibly due to the burning off of sulphur, thus changing the oxysulphide of antimony to an oxide of antimony which combines with Pb and forms the yellow antimonate of lead. At cone 6 on body No. 157, a yellow mat glaze, showing that glaze had been over-fired, was produced. There is no doubt that a good glaze can be produced at cone 5, provided conditions for bluestoning do not exist.

The cost per pound of this flue dust was quoted at 3 cents, which is too high. At cone 02, this glaze was calculated to cost $40.38 per ton or $7.10 per ton cheaper than standard glaze using litharge. At cones 2 and 6, the cost per ton of glaze was $31.90, or $1.17 per ton cheaper than a standard glaze.

The light sprays gave the best results and are as follows:

At cone 02 on body No. B—42 pounds per 1,000 square feet of tile surface.

At cone 2 on body No. 128—66 pounds per 1,000 square feet of tile surface.

At cone 6 on body No. 157—66 pounds per 1,000 square feet of tile surface.

Baghouse Dust. Sample No. 12. As a glaze ingredient, this material introduces considerable carbon, sulphur and volatile impurities. The same careful firing prescribed for the galenas would have to be applied here. At cone 02, a smooth, bright glaze was produced. The only fault was a yellow opacity due to the same cause as that of whiteness in the galena glaze, the yellow tint being due to presence of small amounts of Fe_2O_3. At cone 2, a glaze as good as the standard glaze was produced. The opacity had almost entirely disappeared due to the longer and better heat treatment obtained in this burn. At cone 6, this glaze was the best glaze of the series and was as good as the standard glaze, and furthermore, a good glaze was produced under bluestoning conditions.

The cost of this dust per pound was quoted at 1.4 cents. At cone 02 the glaze was calculated to cost $21.40 per ton, or $26.48 per ton cheaper than standard glaze using litharge. At cones 2 and 6, the cost per ton was $18.40, or $14.72 per ton cheaper than standard glaze.

The light sprays produced the best results and are as follows:

At cone 02 on body No. B—57 pounds per 1,000 square feet of tile surface.

At cone 2 on body No. 128—67 pounds per 1,000 square feet of tile surface.

At cone 6 on body No. 157—40 pounds per 1,000 square feet of tile surface.

Baghouse Dust. Sample No. 14. Just enough of this sample was at hand to carry on the cone 02 study. As a glaze ingredient, the same may be said of this material as of sample No. 12. An immature glaze was obtained at this cone.

Blue Fume. Sample No. 20. As a glaze ingredient, this material introduces considerable sulphur in the form of sulphide, sulphite and sulphate, according to analysis. Therefore, the

same careful and prolonged firing must be practiced when using this material as in the use of galena or the sulphate. At cone 02, an immature glaze was obtained. At cone 2, a glaze as good as the standard glaze was obtained, and almost entirely free from opacity. The cause of this opacity is the same as in the use of galena. At cone 6, a bright surface slightly marred by a bubbling or "boiling" was obtained. This again indicates overfiring.

The cost per pound of this material was quoted at 4.2 cents, which is also too high for a waste-material. The glaze at cones 2 and 6 was calculated to cost $32.60 per ton, or 52 cents per ton cheaper than standard glazes using litharge.

The light sprays gave the best results and are as follows:

At cone 2 on body No. 128—30 pounds per 1,000 square feet of tile surface.

At cone 6 on body No. 157—36 pounds per 1,000 square feet of tile surface.

The point to be emphasized, in using galena or any other impure waste lead material as a glaze ingredient, is that extra precaution must be taken during the heat treatment. The rate of application of heat treatment must be slower than the ordinary heat treatment and an oxidizing atmosphere must be maintained throughout the burn.

Summary. The following is the order of quality of the glazes produced during investigation (using materials to indicate class of glaze):

ORDER

GLAZE	AT CONE 02	AT CONE 2	AT CONE 6
Galena	4th	3rd	failure
Lead sulphate	2nd	1st	failure
Flue dust	1st	2nd	2nd
Baghouse dust	3rd	4th	1st

The lead peroxide was a failure at each burn.

The baghouse dusts could best be used on common wares such as stoneware, glazed sewer-pipe and tile, the range of maturity of

good serviceable glazes lying between cones 2 and 6. In order to produce good glazes, flashing or bluestoning conditions must not exist in kiln at any time of burn. This rule applies to the use of all lead ingredients.

The flue dust would make a successful glaze for glazed brick of all kinds, glazed sewer pipe, tile and stoneware giving the following results:

(a) On bodies (shale or otherwise) maturing at cone 02, an opaque deep red glaze of bright and smooth surface is produced.

(b) On bodies (shale or otherwise) maturing from cone 2 to 6 a bright opaque and yellow glaze is produced.

Galena and lead sulphate can best be used on common wares maturing from cone 02 to cone 2. Trouble, however, would be experienced, more so with galena, if the heat treatment is not oxidizing and carefully regulated.

The following table shows the cost of glazing 1,000 square feet of tile surface by using galena and waste lead materials as the glaze ingredients, and the corresponding gain or loss over the cost of glazing same area by using standard glazes at the corresponding cones according to prices quoted:

TABLE III

GLAZE USING	AT CONE 02			AT CONE 2			AT CONE 6		
	COST PER 1,000 SQ. FT.	GAIN	LOSS	COST PER 1,000 SQ. FT.	GAIN	LOSS	COST PER 1,000 SQ. FT.	GAIN	LOSS
Galena	$0.93	$0.25	....	$0.41	....	....	failure	....	....
Lead sulphate...	1.02	0.16	....	0.63	....	$0.22	failure	....	....
Baghouse dust .	0.61	0.57	....	0.56	....	0.15	$0.48	....	$0.07
Flue dust	0.85	0.33	....	1.05	....	0.64	1.97	....	1.56

The fact that the flue dust turns out a different and better type of glaze than the standard litharge glaze makes it a more valuable glaze material, and I think it would make a very good and practical glaze on the wares mentioned.

The reason for the losses at cone 2 and above is evident from the fact that there is a low Pb content in the glazes employed,

which lowers the amount of litharge to be used in standard glaze. Since litharge is the most expensive ingredient, a decrease in amount used would mean a considerable decrease in cost of standard glaze. Since galena and waste-lead materials have a lower Pb content than litharge, a greater quantity of these materials must be used. It was found that the amount of each sample to be substituted was 1½ or more times the weight of litharge used. It was further found that more of the galena and waste-lead material glazes were used per unit surface in order to obtain the same results produced by a smaller amount of standard litharge glaze. Taking the foregoing facts into consideration, it can readily be seen why the cost of using these materials is greater than in the use of litharge in low Pb glazes for cone 2 or above.

It is evident from this investigation that the employment of waste products, such as have been tested, offers a means of producing on low fire common wares such as glazed brick, sewerpile, drain tile, etc., a dense surface of equal quality as regards service, to that obtained by employing the pure lead pigments. It is further evident, that the use of such materials would make practical the employment of many clays not adapted to salt-glazing, provided the temperature of maturity falls below cone 2.

CAUSE AND DIFFERENTIATION OF SEEDS IN GLASS.

BY ROBERT L. FRINK

In the past few years there has been quite an epidemic of seedy glass throughout the various bottle and pressed-ware houses in this country, and the cause of these seeds or microscopic blisters is, I believe, as yet practically unknown. I have made quite a number of investigations as to the cause and have seen many different kinds of seeds which can readily be differentiated from each other under the microscope, but I can not say yet that I can positively state the cause of each one of these. That is, I can not state as to just what particular error in technique or practice could be assigned to the production of these conditions.

If one allows the factory managers, furnace operators and superintendents the credence of knowledge concerning such causes, which from their long experience, and particular knowledge as to the specific furnace, one might assume they should justly enjoy, he would be firmly convinced that many things from celestial to terrestrial disturbances were causes. At least these have a dominating effect in this direction, to say nothing of the gross effect which manufacturers' errors in raw materials might produce, were it possible for the latter to be of as inferior quality as these gentlemen assume.

A little over a year ago a considerable cut in price was made in soda ash, and the rumor became current that the soda ash manufacturers were using a process different from that of old, which had produced a change in the quantity of Na_2O available in the ash, and, therefore, its cheapness. The supposed change was to many positive proof that therein lay the answer to their troubles and difficulties.

This opinion was firmly fixed in the minds of several since their troubles were coincident with the cut in price, and conditions throughout the factories did seem to indicate that there might be some opportunity and chance of the soda ash beng re-

sponsible Careful analysis of these ashes from various manufacturers showed conclusively that this could not be the case, inasmuch as the soda ash in many instances not only came up to standard of 58 percent Na_2O, but in some cases exceeded this requirement of purity. Several were found to contain as high as 60.2 percent of Na_2O, and rarely, if ever, have they dropped below 56.4 percent. In one or two cases an ash was found to contain in the individual sample obtained but a little over 55 percent of Na_2O, but this material had been for some time exposed to damp atmosphere, and had absorbed from 2½ to 3¼ percent of moisture, which was readily ascertained by ignition.

In any event, a discrepancy in the amount of available Na_2O could not produce so great a change in the composition of the glass or in its melting properties, as would be caused by the variations in calcium oxide and magnesium oxide in the lime used. In one case, where they were making a glass with a formula that would call for approximately 8 percent of calcium and magnesium oxide, the lime which they were using gave to the glass but an average of 4¾ percent of these combined oxides in the proportion of about 2¾ parts of calcium oxide to 1 part of magnesium oxide. The lime used carried 40 percent magnesia. In this instance, I received samples of one car which analyzed but a little better than 72 percent of these two oxides as against 92 to 94 percent in the two preceding cars. This factory has been operating with this lime and under these conditions for several years, and claim that they had never had more than spasmodic troubles with seeds or blisters or any other melting difficulties. Their batch constituents had been varying, however, from 2 to 28 percent., yet as soon as they did get into trouble with seedy glass, they were positive that a difference of not to exceed 4 percent in their soda ash was responsible. It was extremely difficult to make them see that a variation of 30 percent. or more in the lime and magnesia content in their glass would the vary the quantity of Na_2O in excess of that which had been found to be the maximum variation in the soda ash.

I have undertaken to convince the manufacturers, that if there is any trouble arising from material, they must look for it

outside of their sand and soda ash, and while in the past I have been quite firmly convinced that lime and its variability was largely responsible for many of the ills incident to glassmaking, I have in the last few years somewhat modified my censure of this material. I begin to believe, that, while techincally and theoretically it is impossible to make homogeneous and perfect glass without uniform materials, yet it is possible to make and supply a commercially satisfactory product without paying much attention to the lime or magnesia content, providing the mechanical operation of producing the ware does not require consideration of the effect of varying quantities of lime and magnesia upon

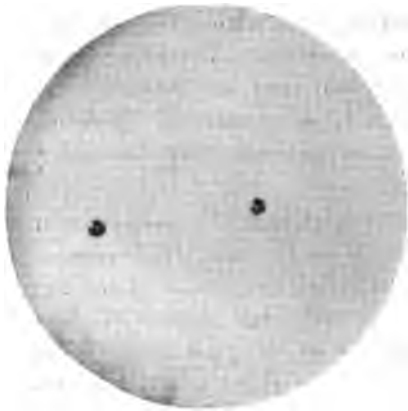


FIG. 1

FIG. 2

the specific heat and viscosity of the glass and upon its behavior in gathering and pressing or blowing.

I have examined a large number of seeds found in glasses especially those produced under known conditions in order to differentiate and positively recognize the various kinds.

I do not claim that I am positively correct in all my conclusions as to the initial cause and character of the seed but I believe, however, that I am correct in all instances except in those otherwise qualified.

If wrong I stand prepared to be corrected; but I trust that those who have criticisms to make will give the privilege and

benefit of their knowledge and experience to the Society by discussions either during our present or future meetings.

A majority of the cases of seedy glass is due to two definite conditions: first, the strenuous and almost heroic effort to obtain increased production, and second, fire and furnace operation. While the second is more or less a factor in the first, there are instances where the two may be operated to produce these causes independently of each other. The factories most troubled with seeds are usually the ones that have installed in the past few years automatic or semi-automatic pressing and blowing machines. Further, it is rarely the case, that they have any specific and definite information as to the quantity of glass melted per hour, or per square foot of melting area within the furnace, previous to the installing of these machines. Therefore, they do not realize or recognize the fact that they are probably demanding from 20 to 50 percent, and in some cases 100 percent, more melting capacity of the furnace than was ever demanded before.

Probably in seven cases out of ten (I candidly believe even more) this is the fundamental cause of seedy glass. This reasoning is justified by the fact that the seeds develop at about the time at which they would be expected when the amount of glass worked out of the furnace and the flow of the glass through the furnace are considered. The character of these seeds indicates that they are composed of minute bubbles of carbon dioxide and carbon monoxide. An example of this is seen in Fig. 1.

Another seed, which is becoming quite common in those factories using semi-automatic machines, is produced from the entrainment of smoke or oil vapor taken in by the punty and deposited in the glass in the gathering. A seed of this character is vastly different from the aforementioned one, in that it is almost always bounded by a yellow or somewhat colored zone, and will often be found to contain minute particles of either ash or soot. These are shown in Fig. 2 and are generally found in trains of two or more.

The seeds shown in Fig. 1 or those made in the melting end of the furnace, will be found fairly uniformly distributed

throughout any one piece of ware, while those illustrated in Fig. 2 will generally be found in local areas, or if uniformly distributed throughout the ware, they will vary in numbers from one piece to the other. These will not reduce in size to any great extent upon cooling, while in some instances those shown in Figure 1 may be quite pronounced while the ware is at a red heat, or just below, but will be almost imperceptible when taken out of the leer.

Another seed, probably the most baffling of all to definitely locate, is due to insufficient melting temperature and fire condition, and is caused by the entrainment of SO_2 or volatilized

FIG. 3

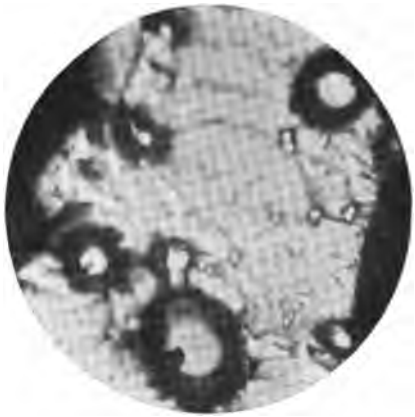


FIG. 4

sodium chloride. Just how this can be produced I can not definitely say, but I am of the opinion that it is caused by the volatilization or incomplete combination of sodium chloride or sulphate, and in consequence the gases of partial dissociation, or the volatilized salt itself, become occluded within the glass under conditions where it can not become oxidized or escape. This might possibly occur under conditions where the batch had been moved beyond the melting temperature zone before combination was effected, or a mass of sodium chloride or sulphate may have become encased within or surrounded by cullet in such a manner as to prevent sufficient chemical action to dissociate the alkalies.

This will be seen in Figure 3 in which the rhombohedral sodium crystals are apparent, lying within the seeds.

Another seed, shown in Figure 4 comes from recombination, *i. e.*, when devitrification has occurred under certain conditions there is produced upon remelting the devitrified glass, a minute quantity of gas. This gas is produced by the cluster of crystals which have been nearly melted and again assumed the amorphous state.

Another seed (illustrated in one of my papers heretofore) was definitely diagnosed and proven to be due to arsenic, but just how such a condition could occur I can not say, it being true nevertheless that when using only 6½ lbs. of arsenic per 1000 of sand, we obtained millions of these small seeds, of a size from a few microns up to 2 or 3 inches in length. In these we were able to positively distinguish the crystals of As_2O_3, and subsequent analysis proved, when the etchings were made, that these seeds were occluded arsenic. They were snow white in color, and were usually found close to the surface.

Figure 5 shows a seed which is produced by the occlusion of air and is caused by a jet of air playing upon a crevice. After the glass had been flowing for a period of time, this crevice became heated sufficiently to overcome conduction of the air, or radiation, and the air pressure was then increased to a point where it passed through the crevice and became entrained in the glass. Such seeds have substantially no effect upon the light rays passing through them, and are almost invisible, at least those which I have been able to produce or definitely differentiate seem to have this appearance, and as shown in the plate, their boundaries only interfere with or disperse the transmitted light rays passing through the microscope condenser and the glass. These are usually found very close to the surface of the finished article, and are generally in trains.

A seed produced by a lack of complete melting or planing of the glass, remains substantially spherical, and also remains incorporated within the glass at various and all depths of the finished piece, while the other seeds are more prone to rise to the surface and in the making of the article will become elongated as shown in Figure 6.

A great deal concerning this subject might be said from a point of supposition, but I have advanced the foregoing with a hope that it may bring forth from others who have investigated the matter a more definite and accurate method of differentiating, or positively identifying not only the seed and its contents, but its cause, and, if possible, an adequate and satisfactory remedy. I believe, however, the remedy, which will successfully eliminate them, lies in restricting the demands on a furnace to that particular furnace's capacity as indicated by its efficiency in developing and supplying heat for the purpose of not only melting and chemically combining the batch materials, but,

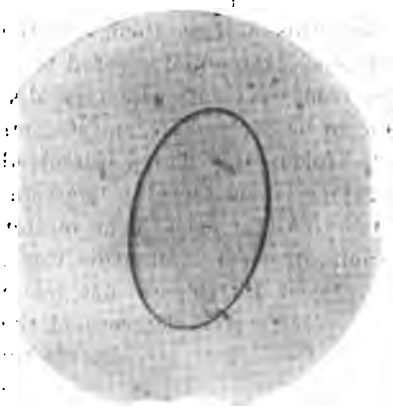


FIG. 5

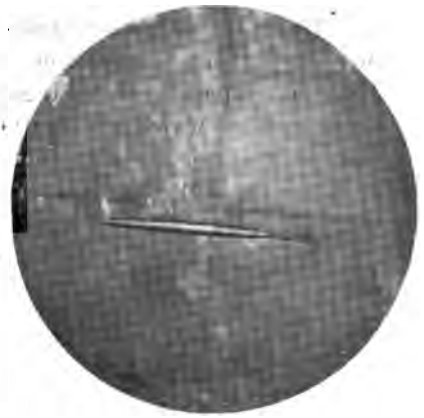


FIG. 6

what is equally paramount, to permit of the efflux of all gaseous constituents. I believe we have a problem which deserves serious and earnest consideration from every glass-furnace operator, superintendent and scientist.

Could we know just what conditions are necessary to obtain a particular kind of glass from a particular design of furnace, or just how to design the furnace to obtain this result and how to subsequently operate the furnace to obtain perfect homogeneity and freedom from gaseous occlusions, we would find that furnace efficiency would be raised from 8 or 10 percent to 15 or 18 percent or perhaps better. This would mean hundreds of

thousands of dollars per year to the glass manufacturers of this country, not only in fuel but in increased production. The homogeneity and quality of ware would then be such as to pass through the leers, go out on the market and withstand normal usage without any "come-back" for breakage, crizzling, cracking, etc.

DISCUSSION

Mr. Silverman: Mr. Frink's differentiation of the various types of seeds is exceedingly interesting, and if we could determine what the seeds contained there isn't any question but what we should be able to solve some very serious problems.

There are only three causes for seeds, as I see them. In the first place, there is volatile matter, such as arsenic referred to in Mr. Frink's paper. Second, gases from materials which are dissociating, and which will continue to be evolved so long as that material has not been completely broken up. Third, dissolved gases. I think this factor is one which is considerably more important than we have thought in the past at least. The matter of solubility in glass is quite serious in certain scientific work. Dr. F. C. Phillips, of the University of Pittsburgh, has taken glasses, crushed them in a vacuum mortar and determined the amount of gas which was occluded or in solution. It is perfectly clear, from our experiments with ordinary materials, that the amount of gas dissolved will, in most cases, decrease with increased temperature, and that if a glass cools and is subsequently reheated the gases which have been absorbed or dissolved, are going to separate, so there is the third type of seed depending upon reheating.

However, I think we can eliminate all of these if the viscosity of the metal is sufficiently low and we give plenty of time for melting. Planing and viscosity are the big factors.

Mr. Frink: There is no question but what Dr. Silverman says is true in part; however, I must differ with him in practice. There is absolutely conclusive proof that there are more than three causes for seeds. In the first place, decomposition is one. However, there is not only an occlusion of gases, perhaps due to

lack of complete melting, but there is also another condition which is found in high temperatures. The higher the temperature, the more of that condition is found. If you get up to a temperature where the glass begins to boil, or there seems to be a separation of the more basic constituents of the glass, you will occlude much more gas than you did before.

In speaking of determining gases within glass, recalls to mind some experiments made some few years ago, in which there did not appear to be any question but what there were gases within the glass, but nevertheless, when it was melted in an electric furnace under vacuum it came out with substantially the same tenacity, the same index, and apparently the same all the way through. That would seem to refute the idea that if there were gases in there which could be eliminated by planing, they would have been brought out. In my opinion, any gas that is occluded will stay in that glass throughout the whole period. It must be a gas that is foreign to the glass, in order to plane up or cause a distinct seed that will be eliminated.

There is another point: If you will take a piece of cold glass and put it upon another piece of cold glass, gradually raise the temperature of these by putting them in an electric furnace up to 800°C. or 900°C., and then admit air into the furnace, that would soften the glass to a point at which it would pour together and adhere. Now raise the temperature to 1200 or 1400°C., and there will be seeds between the plates and in these plates. That would seem to indicate then that there is a seed.

Mr. Silverman: Mr. Frink has corroborated my statements absolutely. The air which is introduced between glass layers will remain there, providing the viscosity of the glass is not sufficiently low to permit its escape. The seeds which form when glass is reheated consist of the absorbed or dissolved gases which cannot escape because of the viscosity. The gas which is given off when the temperature is at boiling point is the gas resulting from dissociation of materials at that high temperature.

Mr. Frink: While perhaps I wish to corroborate what Mr. Silverman says, nevertheless he speaks of viscosity and the boiling point as being the determining factor of the elimination of

seeds. That is not practical at all, because when we get up into high temperatures viscosity doesn't cut much figure; when you are getting say an ordinary bottle glass, you can heat it just as hot as it can be heated, you will not get rid of these seeds, they will stay there. There seems to be one determining factor in actual practice, which cuts more figure than viscosity. Because I have absolutely seen in tank furnaces glass at temperatures of 1450°C. at the planing end of furnace. If we had a high stock pressure, we could then plane these gases perhaps, but we can push up the temperature where we have a mind to, it cuts no figure, we have got to have some sort of pulling action on the surface, have got to make it move on the surface in order to get the underneath started. It is not a corroboration at all, because viscosity is a filtration of temperature plus ingredients.

Mr. Silverman: What Mr. Frink says is but an application of Henry's Law of Partial Pressures to gases.

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